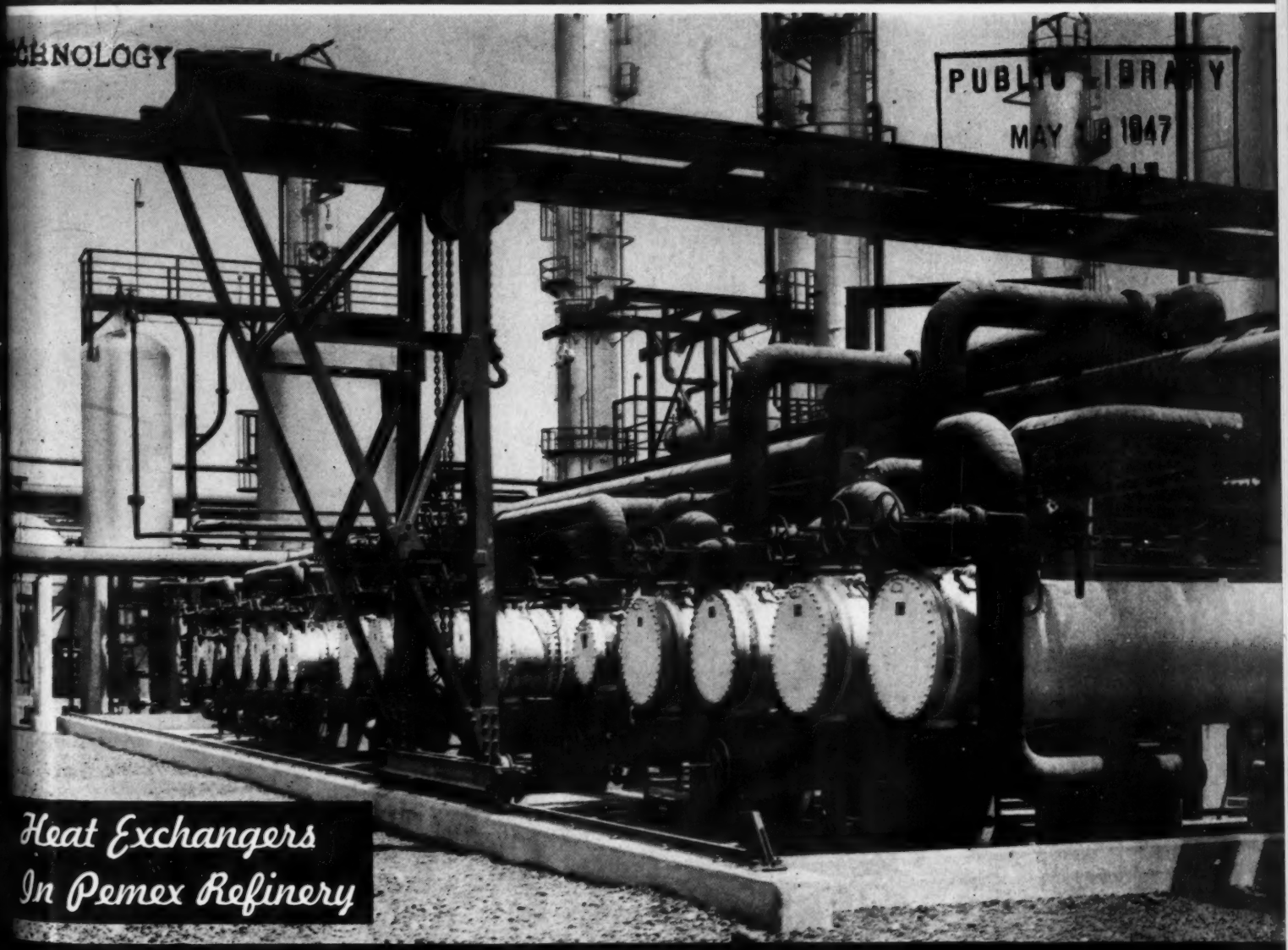
PETROLEUM PROCESSING

VOLUME 2, NUMBER 5 MAY, 1947



Heat Exchangers In Pemex Refinery

FORMERLY MONTHLY TECHNICAL SECTION OF NATIONAL PETROLEUM NEWS

TCC REQUIRES MINIMUM MAINTENANCE...

not only in money, but in man-hours!

In catalytic cracking, it's the over-all on-stream efficiency that counts. And that depends not only on long runs but on short down time for turn-around.

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These are typical—not extraordinary—examples of how TCC's basic simplicity of design pays off in minimum maintenance. Its shorter turn-around time saves money and man-hours. This is of particular advantage in refining operations of relatively small size, where a single catalytic unit is the only source of high-quality fuel. It is easy for such a refiner to build up, in advance of turn-around, a sufficient backlog of catalytic motor fuel to keep him in production throughout the brief turn-around period.

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PETROLEUM PROCESSING

Of Crude Petroleum and Natural Gas
For Fuels, Lubricants and Petrochemicals
REFINERY OPERATION, MAINTENANCE, EQUIPMENT, DESIGN

FORMERLY MONTHLY TECHNICAL SECTION OF NATIONAL PETROLEUM NEWS

COMING MEETINGS

May

1-2, Society of Automotive Engineers, Personal Aircraft Meeting, Hotel Lassen, Wichita, Kansas.
17-24, International Petroleum Exposition, Tulsa.
20-21, API, Lubrication Committee, Los Angeles.
21-24, American Society of Mechanical Engineers, Oil and Gas Power, National conference, Cleveland, Ohio.
26-29, American Society of Mechanical Engineers, Aviation Division, Conference, Los Angeles.
27-29, Liquefied Petroleum Gas Association, Annual convention, Sherman Hotel, Chicago.
27-30, Texas College of Arts and Industries, Annual short course in Gas Technology, Kingsville, Texas.

June

1-6, Society of Automotive Engineers, Summer meeting, French Lick Springs Hotel, French Lick, Ind.
2-3, American Petroleum Institute, Refining Division, Jefferson Hotel, St. Louis.
5-6, Pennsylvania Grade Crude Oil Association, Annual meeting, William Penn Hotel, Pittsburgh.
12-14, American Chemical Society, 10th National Organic Chemistry Symposium, Division of Organic Chemistry, Boston, Mass.
15-20, American Society of Mechanical Engineers, Annual meeting, Chicago.
16-20, American Society for Testing Materials, 15th Annual meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.

July

29, API, Lubrication Committee, Executive Committee, Skytop Inn, Skytop, Pa.

THIS MONTH'S COVER . . .

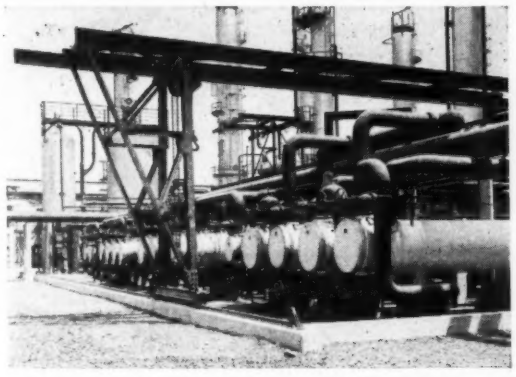

Photo Courtesy Arthur G. McKee & Co. and Petroleos Mexicanos

Fuel-hungry Mexico, in its recently modernized Petroleos Mexicanos refinery at Atzcapotzalco, near Mexico City, has made an extensive use of heat exchangers. Simplified, safe, and efficient maintenance of heat exchange equipment is provided by the traveling, overhead crane. The first article to be published describing in detail the various installations at the Pemex refinery begins on page 334 of this issue of PETROLEUM PROCESSING

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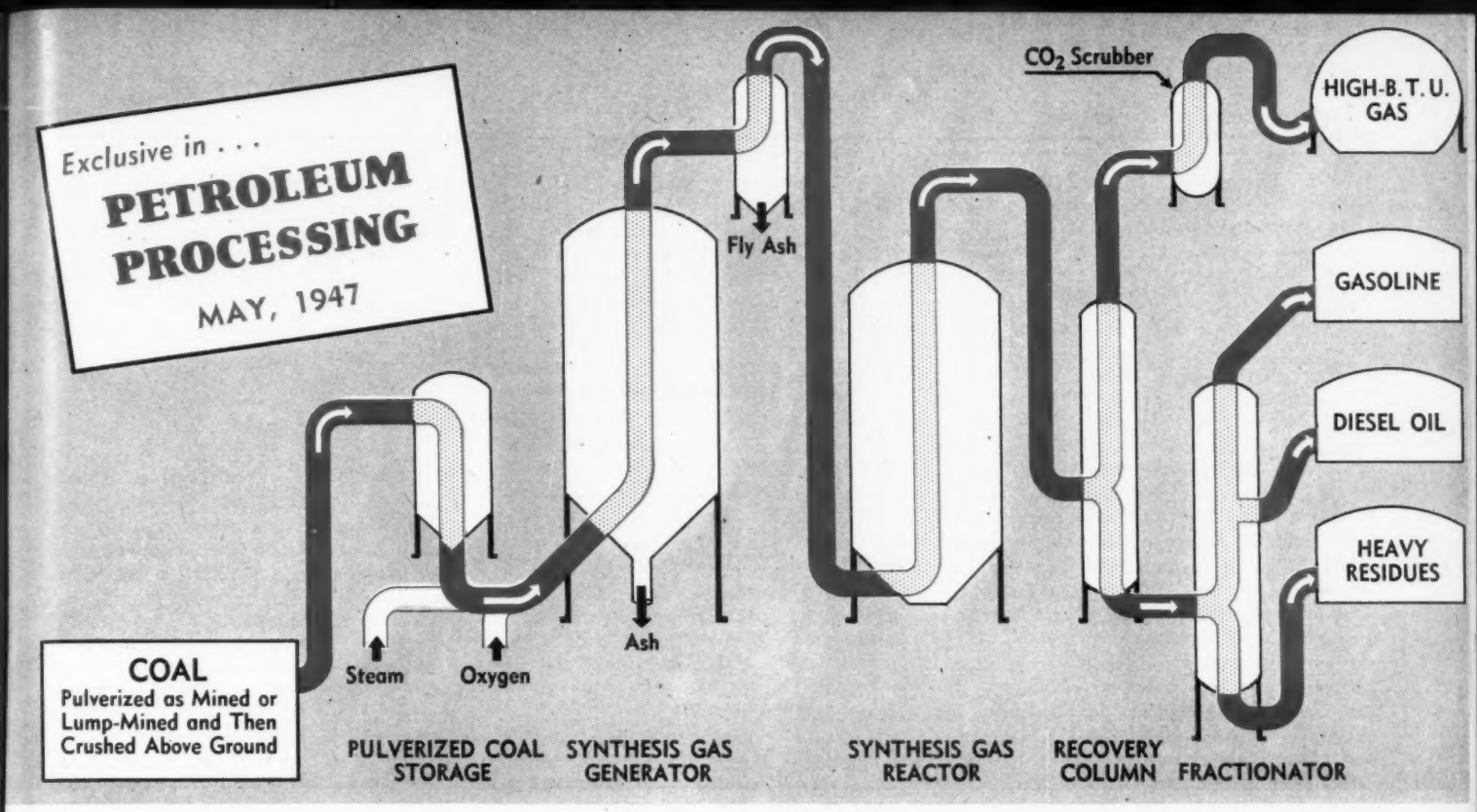


Here's one possible version of how the oil refinery of the future might look—operating on coal instead of crude petroleum

REFINERIES of the FUTURE

Processing Coal into Liquid Products May Be Practicable in a Few Years

By WILLIAM F. BLAND
Engineering Editor
PETROLEUM PROCESSING

REFINERS of the not-so-distant future may include in their possible range of operations the processing of liquid fuels and other products from coal, as well as from natural gas and crude oil as at present.

Technologists in the petroleum industry have long recognized that coal represents the nation's greatest natural energy resource and that eventually coal might be synthesized into liquid products to supplement our crude oil reserves. Until recently, however, no one came up with the answers to "How much?" or "How soon?"

On March 25, Standard Oil Co. (N. J.) and Pittsburgh Consolidation Coal Co. jointly announced a program for gasifying coal and converting it into liquid fuels, high-BTU gas and chemicals. It is said that commercial gasification and synthesis plants costing $120,000,000 or more may result from this work and it is believed the program will greatly advance the day when it will be commercially practicable to process coal into liquid products.

Research groups of these two companies, the largest in their respective industries, have been carrying on studies on the gasification of coal for some time. A $300,000 demonstration size pilot plant to continue the studies and bring the process to a commercial basis is now being planned. It will be located at Library, Pa., near Pittsburgh, and is expected to be ready for operation by the end of 1947.

The work these two companies are engaging in is primarily concerned with taking pulverized coal and burning it under controlled conditions and in the presence of steam and oxygen to produce synthesis gas — carbon monoxide and hydrogen. This gasification step would utilize Jersey Standard's fluidized solids technique, worked out primarily by Standard Oil Development Co. (Jersey's research subsidiary) for the Fluid Catalytic Cracking process.

About 50 tons of coal a day would be consumed by the pilot plant, which is expected to yield around 2,400,000 cu. ft. of gas suitable for synthesis work, nearly 50,000 cu. ft. per ton.

Once the synthesis gas is formed and purified it can be converted to liquid products by the conventional German Fischer-Tropsch reaction, as further developed and improved by various U. S. oil and research firms. Standard Oil Development has also done work on the application of the fluidized technique to this operation, and it is being further developed in 25-30 pilot plants, ranging in size from 2 oz. to 150 gal. per day capacity.

The fluidized solids technique is familiar to all refinery technologists who have studied the Fluid Catalytic Cracking process. As applied to coal gasification it operates in much the same way as it does in the "cat crackers," except that coal takes the place of the catalyst, and oxygen and steam are introduced instead of oil vapors. The powdered coal reacts with the oxygen and steam to form the desired synthesis gas.

Commercial plants costing as much as $120,000,000 per unit may result

from this project, in the opinion of Pittsburgh Consolidation engineers, and could be operating in three to four years.

"A commercial plant for making liquid fuels and a high-BTU gas," predicted Joseph Pursglove, Jr., Pittsburgh Consolidation's vice president in charge of research and development, "could be located within 25 miles of Pittsburgh, near one of the company's large coal tracts, and we hope might be ready for operation by 1950-51. One single large plant of the size being considered could yield a gas of high heat value in quantities equal to the output of the Big Inch and Little Inch pipelines, as well as creating a local source of gasoline, Diesel and other fuel oils, and a certain amount of alcohols."

The financing of such a project, according to George H. Love, president of Pittsburgh Consolidation, "might be done as a joint undertaking by industries closely interested in such an operation."

Why Jersey Looks to Coal

Jersey Standard has two principal reasons for seeking to perfect the production of synthetic gasoline from coal, according to Robert P. Russell, president of the Development Co. "First," he stated, "it would assure the U. S. of an enormous potential reserve of liquid fuel. The second is that the cost of finding oil and its production is mounting and will probably continue to rise."

While the demand for petroleum products is increasing each year, Mr. Russell added, the company's geologists are confident that the industry's crude reserves will be as large in this country 20 years from now as they are today.

"However," he said, "coal is by all means our greatest source of energy. Commercial reserves of all grades of coal total about 3.18 trillion tons. If half that can be used for synthesis, coal could represent a potential gasoline reserve, for example, of 3.7 trillion bbls., or enough to last more than 3000 years."

Coal Ripe for Modernization

The coal industry itself is ripe for modernization—and the petroleum industry appears to be in a good position not only to show coal how to effect that modernization but also to take the initiative and lead the way.

Fortune magazine recently ran a series of articles on coal, and figuratively gave the industry an unrelenting "raking over the coals." Said *Fortune*: "Coal is a laggard—economically, socially, and technically."

Elsewhere in the articles it is pointed out that the coal industry "cannot, over the long range, make any money at all" and had an "aggregate net loss of over $350 million between 1925 and 1940;" that "in 1910 it supplied 90% of all energy markets, and now supplies only 46%;" that it is "an industry of over 6000 different producing companies. . . consistently competing *against itself* in terms of price cutting and scarcely at all against industries with technologies more active than its own," and that it "does its day's work with such backward inefficiency that it cannot feed its own self well."

Mining Process Is Discontinuous

Fortune criticizes coal for, among other sins, its lack of technology, research and mechanization. It is an industry operating on a "*dis*continuous process," and saddled with a "materials-handling philisophy."

Oil is more closely akin to coal in chemical composition than any other large tonnage material on the earth—and yet the two industries are as wide apart in their method of operation as the U. S. and Russia are on their peace treaty with Germany.

The coal industry has been content for the most part to bring its product out of the earth and then forget about it. It has done little if anything to "process" or "refine" coal and take advantage of the treasure house of complex chemicals stored in coal's molecular structure. It leaves the marketing of its product to others.

Many oil companies, on the other hand, not only produce their raw material but also refine and market it. They have developed integrated operations, and have learned how to manage each phase for the mutual profit and advancement of the whole.

The Revolution Has Started

Coal hasn't been given up as an entirely lost cause, however. "There are now some grounds," says *Fortune*, "for revived hopes that engineering brains may set forth to the rescue of the coal industry and of coal mining and utilization. . . . A major technological revolution . . . is coming about through the pressure of the brains and money that lie in the petroleum industry."

The Jersey Standard and Pittsburgh Consolidation program for joint research on coal gasification and liquid fuel synthesis is the opening shot in that "revolution."

The biggest thing that the amalgamation of oil and coal interests can do to coal is to eliminate the "materials handling" idea now holding it back. Coal boasts, quite accurately if short-sightedly, that it is "the biggest bulk industry in the world." As presently utilized, coal is mined by the lump, hauled to the surface, cleaned and sorted, and eventually delivered, by tortuous and devious means, to the consumer—*still in lumps*. Nothing has been done to it, expect possibly a minor treatment to keep down the dust. And for every ten tons of coal that the consumer buys he also pays for the privilege of disposing of about one ton of ashes.

Coal gasification right off the bat eliminates most of the materials handling problem. After the gasification and synthesis, you have only easily-handled fluids—high-BTU gas, and liquid gasoline and oils. Pipelines, direct to the consumer in the case of the gas, solve the transportation problem. The ash problem was taken care of in the gasification step.

As for the materials handling problem up to the gasification point, three possible solutions are in sight:

1. Mine coal as at present by the lump, bring it to the surface, and there pulverize it prior to gasification.

2. Mine the coal and pulverize it below ground, blowing or exhausting the pulverized coal to the surface gasification plant.

3. Gasify the coal right in the ground, by burning it under controlled conditions and with the introduction of steam and oxygen to yield the desired synthesis gas.

The first is really no solution at all. It is an expedient for present operations, until more is known about methods two and three.

Pulverizing Increases Production

Underground pulverizing and suction removal has already been tried and proved—35 years ago in one of Big Steel's mines. The objection at that time was that the crusher wasn't very selective and ground up slate together with the coal, to which the consumers objected. Slate, however, is not an objection in the gasification process, since it merely adds its bulk to the ash which is removed. Using this method, it has been claimed, one operator could produce 100 tons of coal a day, compared to a present rate of 5.1 tons.

Underground gasification or burning the coal "in situ" offers the most promising future, it is believed, since it eliminates entirely all of the mining work, except for small access tunnels to start the fires, admit steam and oxygen and remove the gases. It has the additional advantage of permitting utilization of narrow coal seams, ordinarily too thin for mining.

Underground Gasification Not New

Underground gasification was suggested as long ago as 1868, and in 1912 the British scientist Sir William Ramsay argued that it was inefficient to dig coal out of the ground and then burn it on the surface. In 1929 Leo Ranney, then working for Jersey Standard, came forward with more definite plans on the subject—but Jersey was more interested in oil than coal. This was the same Ranney who more recently has startled the oil industry with his "oil mines" in Pennsylvania.

The Russians have probably done more with underground gasification than anyone else, and recent reports indicate that they have been carrying out the operation on a commercial scale for the past six or seven years.

In this country the Bureau of Mines has finally gotten around to devoting

part of its $30,000,000 project for research on synthetic liquid fuels to underground gasification. On Jan. 21, in cooperation with the Alabama Power Co., the bureau set afire a selected seam of coal 30 ft. below the surface at Gorgas, Ala., 20 miles from Birmingham.

The seam had previously been isolated from an active mine. Two horizontal entries, 6 ft. in width, were dug into the 2½ ft. seam and connected at the far end with a crosscut. Concrete pipings were installed at both ends of the two entries of the U-shaped structure. Several holes were core-drilled from the surface into the coal seam to take gas samples and temperature readings. Using a compressor, air was blown into one entry as gas emerged from the other.

Combustion Was Maintained

In reporting on the project, Dr. R. R. Sayers, director of the Bureau, stated that "no difficulty has been encountered in maintaining combustion. . . however, the resistance resulting from roof falls and other undetermined causes prevented an air flow sufficient to obtain the desired temperature in the burning coal and the quality sought in the gas."

One of the essentials in the production of a good quality synthesis gas is a high effective reaction temperature to insure the proper reduction of carbon dioxide to carbon monoxide, and the dissociation of moisture to result in hydrogen and additional carbon monoxide formation.

Later in the Bureau of Mines experiment, oxygen was used to enrich the air in an effort to increase the temperature. However, technical restrictions on the oxygen supply limited it to 200 cu. ft. per min., which still was insufficient to raise the operating temperature to the required level.

"Nevertheless," the Bureau reports, "the use of oxygen indicated that under more favorable conditions synthesis gas might be produced continuously." The Bureau also believes that "the production of synthesis gas by alternate air blasting and steaming has been indicated to be a distinct possibility." This may be tried in later phases of the Bureau of Mines experiments in coal gasification in the Alabama Power Co.'s mine.

How Much Coal Is There?

As to how much coal we have and what it represents in terms of oil and gas, the consensus is that coal could supply all our fuel needs for at least several thousand years—at present consumption rates.

It is estimated that this country has a reserve of roughly 3.2 trillion tons of coal. We are presently using it at the rate of about 600 million tons a year. We are also consuming annually about 1.7 billion bbls. of crude oil and 4.0 trillion cu. ft. of natural gas.

According to one source, it would require 1.9 billion tons of coal annually to supply all the fuel needs now taken care of by coal, oil and natural gas. That figure is arrived at in two steps.

First, assume that all present users of oil and gas were supplied with similar products from coal. The energy equivalent of the present oil and gas consumption is about 550 million tons of coal. But since the thermal efficiency of present conversion methods is only about 50%, it would require 1.2 billion tons of coal to reproduce in liquid and gaseous form the same amount of energy as is now consumed in the form of oil and natural gas.

Second, assume that about 200 million of the 600 million tons of coal now consumed annually would continue to be used as coal. The present users of the remaining 400 million tons would switch over to gas made from coal. But since present gasification methods are only 80% efficient, it would require 500 million tons for their needs, or a total of 700 million tons.

Adding the 1.2 billion and 700 million together we get the 1.9 billion ton figure and dividing that into our coal reserves of 3.2 trillion tons gives us a fuel supply from coal sufficient for 1600 years.

There are, of course, several important factors not taken into account in these figures. For one thing, we can be sure that the thermal efficiency of conversion from coal to liquid and gas will improve considerably over its present 50% level. Also, underground gasification will increase our coal reserves above the present 3.2 trillion tons by making it possible to utilize many deposits now considered too thin to be worked.

As to the cost to the consumer, you can find as many estimates as there are estimators. Even at the present stage of development, however, it looks like a gallon of motor gasoline from coal could be sold at a price not much greater than the present 22c/gal. country-wide average for conventional gasoline.

With additional research by private industry to increase the thermal efficiency of conversion and to decrease the raw material cost by underground gasification, the finished product cost can be expected to drop—perhaps even below the 22c/gal. figure.

Private Enterprise Leads in Research

The joint research on coal gasification by Standard Oil Co. (N. J.) and Pittsburgh Consolidation Coal Co. is further evidence to dispute the Bureau of Mines' implied if unspoken claim that private industry is doing nothing at all to safeguard this country's oil supply, and that the Bureau must therefore have $30,000,000 or $60,000,000 for synthetic fuels research.

The extent to which the Bureau has gotten across the idea that it has done all the research on this subject was amply demonstrated in one newspaper columnist's comments on the Jersey Standard-Pittsburgh Consolidation project: "Both organizations have been observing carefully the operation of pilot plants by the Bureau of Mines, which has improved upon the German process in use many years ago."

We don't doubt but what the companies have been watching the Bureau's work, but the implication is that the Bureau has been carrying on a lot of work to watch.

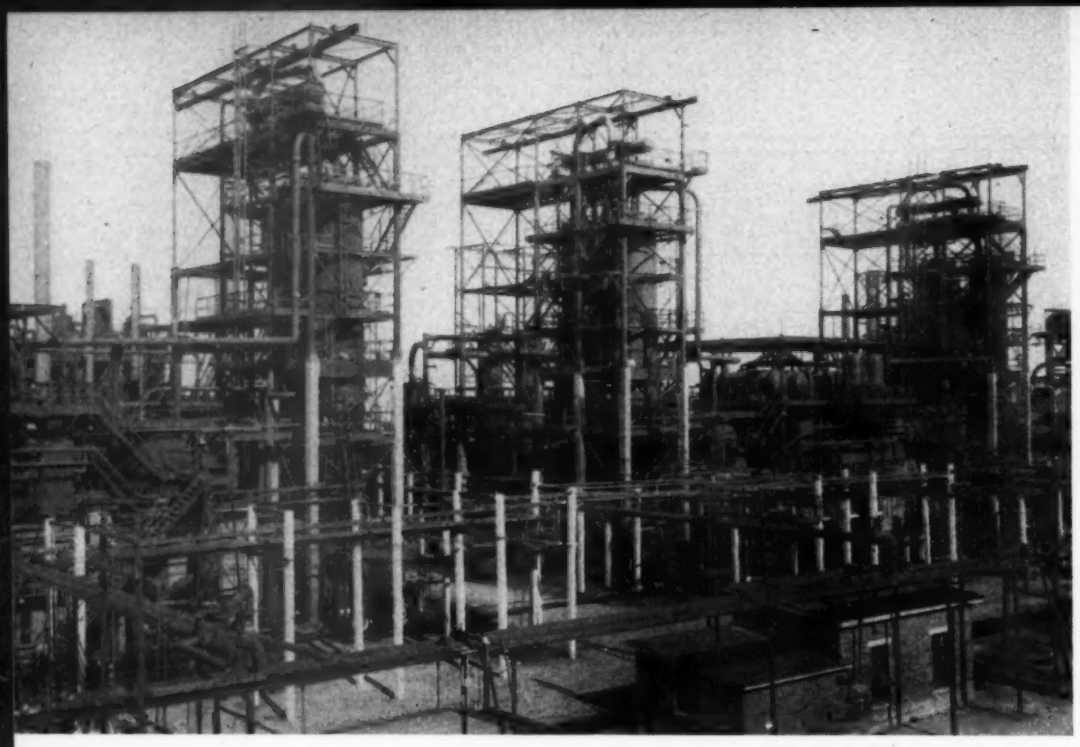
Quite to the contrary, the Bureau has devoted terrifyingly little of its present $30,000,000 research undertaking to improving upon the German process which it is contemplated to use in the present project—the basic German Fischer-Tropsch reaction.

Instead, the Bureau has been concentrating its research efforts on the hydrogenation of coal, with secondary emphasis on recovering oil from shale. Only recently, after private industry had already developed commercial methods of synthesizing gasoline from nautral gas, did the Bureau seriously turn its attention in that direction—and ask for another $30,000,000 to carry on the work.

Eric Hodgins, a chemical engineering graduate of Massachusetts Institute of Technology, writing in the April *Fortune* on "The Fuel Revolution," roundly criticizes the Bureau for its synthetic fuel program:

"As to hydrogenation," he states, "its costs are against it. The hydrogenation revolution that Bergius started in Germany in 1910 seems to have served its purpose and burned itself out. Standard of New Jersey holds the major patents on hydrogenation in America, but Standard's Murphree calls the issue dead. . . . the Bureau of Mines . . . is doggedly determined to give hydrogenation a final chance to prove itself in the face of its new competition from Fischer-Tropsch. But the U. S. oil industry, which has to spend its own money, has dropped hydrogenation cold.

"As to shale, Texaco owns the largest holdings of shale land of any oil company in the U. S., but it has stopped research work on oil-shale recovery. 'If you're going to dig a ton of rock,' says Dobie Keith (president, Hydrocarbon Research), 'it might as well be burnable rock.' It looks as if that one sentence were the epitaph for shale." —W. F. B.



General view of a group of thermal coil and drum cracking coils which were adapted to Suspensoid catalytic cracking at the Sarnia, Ontario, refinery of Imperial Oil Ltd.

Photos courtesy Imperial Oil Ltd.

SUSPENSOID CATALYTIC CRACKING

Low Cost Operation Applied to Existing Thermal Cracking Units Provides Small Refiners with Inexpensive Means for Improving Research Octane Rating and Sensitivity of Their Motor Gasolines

By ROBERT L. PURVIN
Consulting Chemical Engineer

THE gasoline manufacturing facilities of many small refiners are being strained today to produce motor fuels meeting current antiknock rating requirements. It appears likely that, when tetraethyl lead becomes more plentiful, octane numbers of ethyl and regular brands may be further increased.

An even more serious change taking place is the emphasis being placed in some quarters upon higher Research octane values and upon a greater gap between Research and Motor octane numbers to increase the so-called "sensitivity" of the motor fuels marketed. This latter requirement depends entirely on the chemical nature of the base stock available. It cannot be met by use of an additive, but can be achieved by severe cracking as is found in the catalytic cracking operation.

It is evident that, if the small refiner is to compete in this new market for high octane motor fuels, he must have the facilities to make the necessary base stocks. This can best be achieved by a catalytic cracking unit replacing the thermal cracking operation, but this decision is a difficult one particularly for refineries of under 4000 b/d capacity, since their present entire plant investment in many cases is approximately half the cost of a catalytic cracking unit to replace the thermal coils.

A great deal of work has been done on the development of an inexpensive catalytic unit within the reach of refiners who require a cracking unit of 1000 to 3000 b/d capacity. Of the processes that have been suggested, the Suspensoid catalytic cracking process, developed at

The Author

Dr. Robert L. Purvin was born and reared in Texas, and was graduated from the University of Texas in 1937 with a B. A. degree. He received a B. S. degree a year later, and graduate study at Massachusetts Institute of Technology led to a D. Sc. degree in 1941.

His first job was with Humble Oil and Refining Co. in 1941, where he started in the technical service division as a process engineer concerned with general refinery technical service. He was transferred to development work on butyl rubber, and later assisted in manufacturing operations. He opened an office as consulting chemical engineer in Dallas in 1946.

the Sarnia refinery of Imperial Oil Ltd. of Canada, provides gasolines with substantial Motor and Research octane number increases for a relatively small outlay of new capital. The available thermal cracking facilities are utilized to the greatest extent and it is only necessary to make a few changes and add a small amount of auxiliary equipment.

One Revision was under $80,000

A recent study of a small East Texas refinery indicated that the entire conversion cost would not exceed $80,000. Such small quantities of catalytic clay, such as Super Filtrol, are required that it can be used on a once-through basis and, therefore, expensive regeneration equipment is not required. Only very active clays can be used, but it has been found that spent Super Filtrol from lube oil contacting is still active enough to be satisfactorily utilized in the catalytic cracking operation.

It has been demonstrated on a pilot plant scale that the synthetic catalysts are considerably better than the natural clays, but without regeneration their cost makes their present use prohibitive. The Imperial refinery at Sarnia now has four 5000 b/d and one 9000 b/d cracking units in operation utilizing spent clay.

The entire development of the Suspensoid catalytic cracking process has been based on the desire to use as much of the available thermal cracking equipment as possible with the minimum of additional expenses in new equipment. Originally, it was attempted merely to inject clay into the regular thermal coil under the same conditions of temperature and pressure which then existed in the thermal units. However, it was not until the temperature was increased and the pressure adjusted to insure complete vaporization of the stock leaving the coil that a definite improvement in gasoline quality was observed. In essence, it was seen that the process bore some relation to the Fluid catalytic cracking operation.

Permits Higher Temperatures

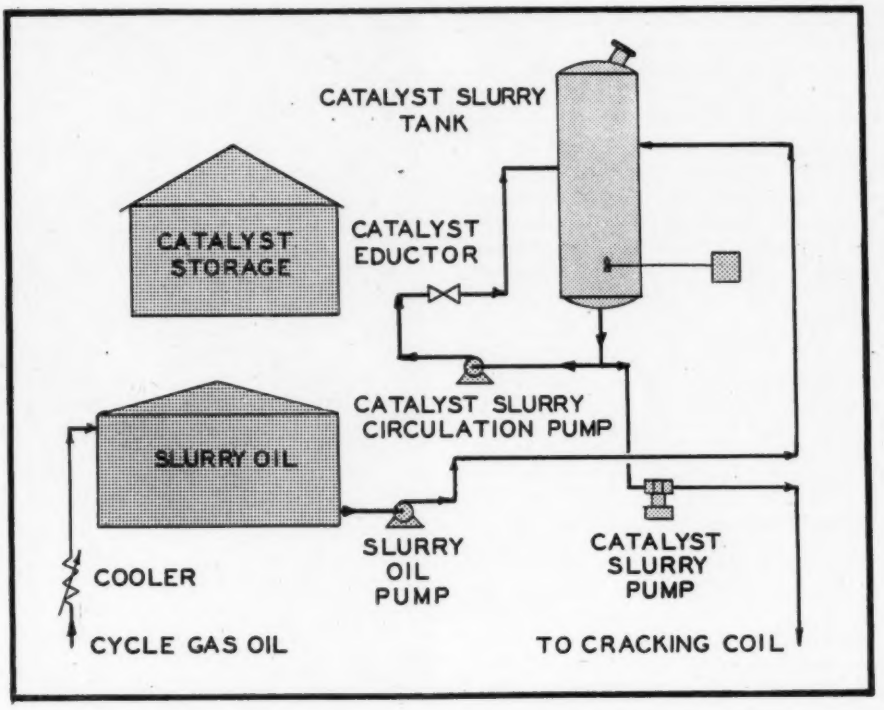
The studies which were carried on principally by Imperial Oil Ltd. showed that the clay served not only as a catalyst but also enabled the coil to operate successfully at the higher temperatures which were required.

It was shown that non-catalytic clays would permit operation at a slightly higher temperature, but the octane number improvement was not as great and the loss in lead suceptibility considerably greater than where the catalytic type clay was used. Further studies on the process showed that where heavy gas oils were used, water or naphtha injection would permit complete vaporization at lower temperatures and higher pressures.

In this connection, it was found that heavy naphtha processed in the Suspensoid operation in conjunction with light, medium, or heavy gas oils was reformed to a gasoline with an octane number approximately the same as the pressure distillate from the gas oils. Yield studies indicated that the quantity of gasoline produced by combined Suspensoid operation was greater by approximately 5% than where Suspensoid gas oil cracking and thermal reforming were carried out separately.

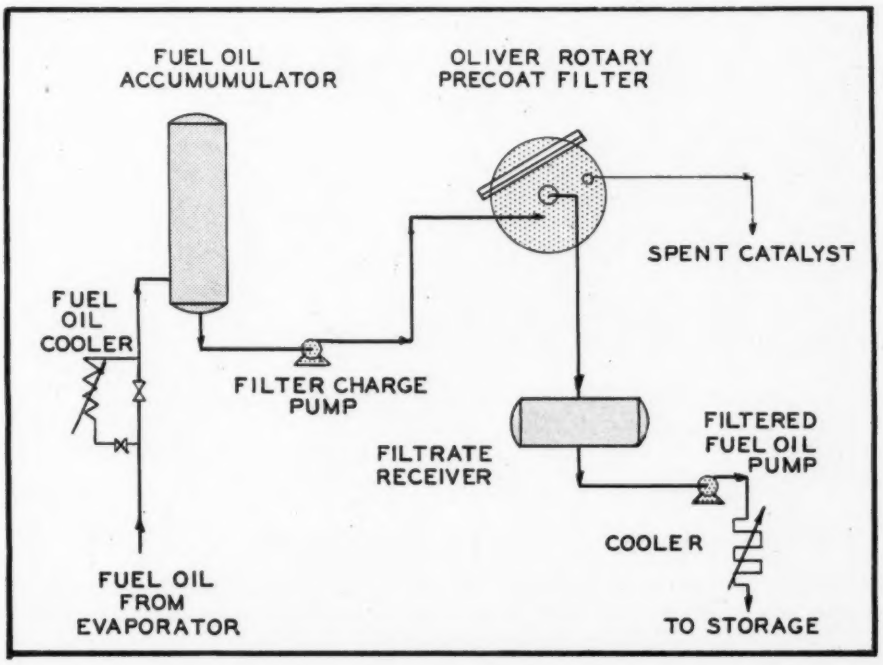
This latter development should be of particularly great importance, as the average small refinery has no facilities for reforming its heavy naphthas and therefore, these must be worked off in gasoline solvents, or kerosine. In this manner, this stock can be up-graded considerably from its present outlets.

As a result of the catalytic effect of the clay and the higher operating temperatures, the conversion per pass is in the order of 80 to 90% based on coil charge. Due to this high conversion, the quantity of recycle is reduced consider-



ABOVE—Flow diagram of the Suspensoid catalyst slurring equipment

BELOW—Flow diagram of the fuel oil filtering equipment



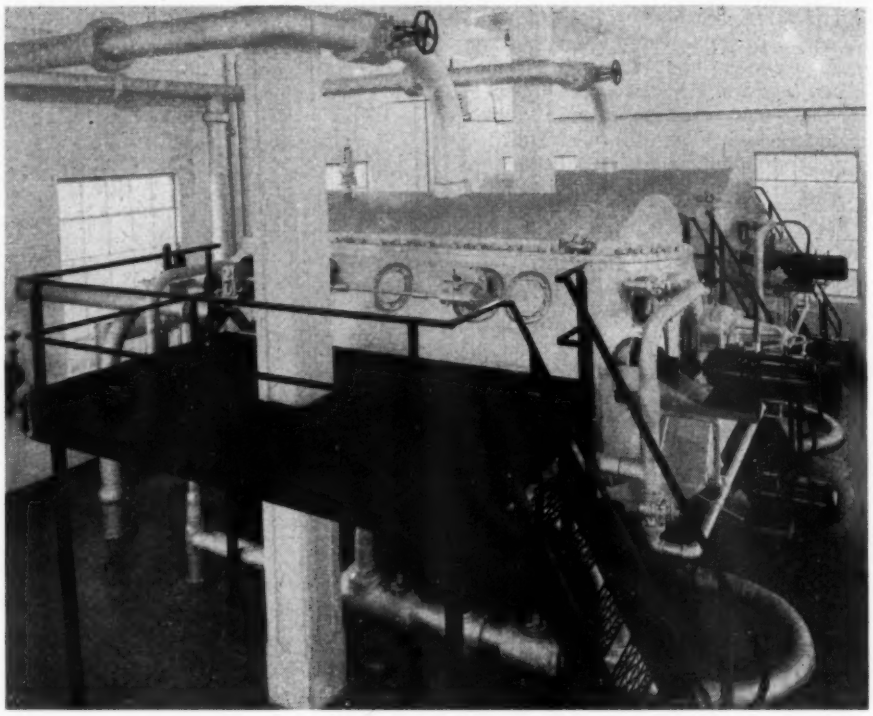
ably and, even though a greater heat input per gallon is required at a higher temperature level, the total heat load on the furnace is generally less than for the comparable thermal operation.

In each individual case this can be determined by a comparison of the heat requirements for the thermal cracking operation at relatively low temperature with high recycle with the heat requirements for a high temperature Suspensoid operation with low recycle.

In many cases, therefore, it should be possible to increase the fresh feed to the cracking operation without overloading the available furnace. Heavy naphtha may thus be added for reforming without reducing the amount of gas oil or reduced crude charge to the unit.

Built Around Thermal Units

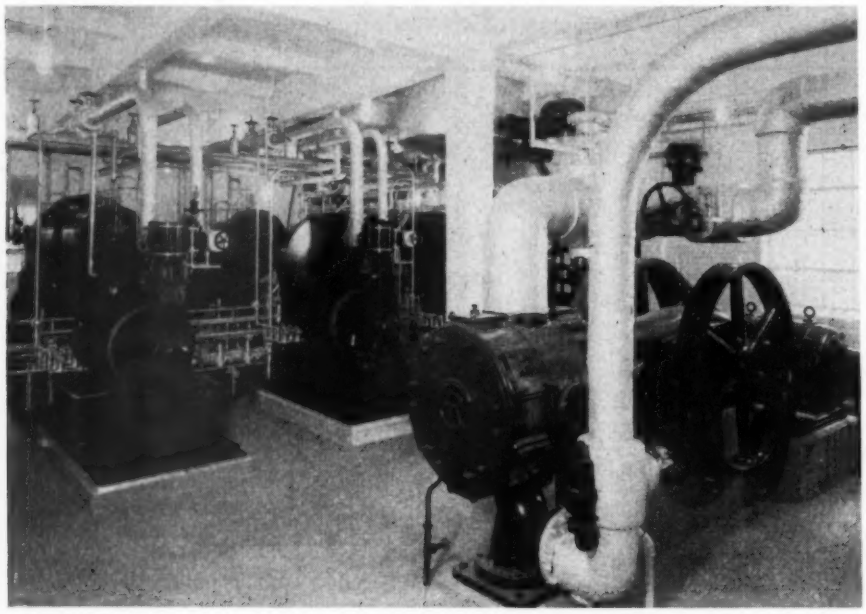
As pointed out above, the Suspensoid catalytic cracking system is built around standard thermal cracking units with the addition of clay slurrying equipment, slurry injection equipment, fuel oil filtration facilities and clay disposal equipment. Changes to the thermal unit itself are relatively simple: if the present process is a coil-only operation, it is merely a matter of adjusting the number of tubes to secure the proper V/V/hr. In the case of a tube and tank unit, the reactor is by-passed and the coil is adjusted in a similar manner. In consideration of higher operating temperatures, the last 10 to 15% of the tubes in the radiant section should be 4-6% chrome and ½% molybdenum. In those units where there is a considerable amount of heat exchange between the evaporator vapors or bubble tower vapors and fresh feed or crude, it is necessary to make some adjustments as the recycle with Suspensoid is considerably less and, therefore, additional heat to these streams must be provided elsewhere.



Rotary filters used for removing spent catalyst from cracked fuel oil

The process, as applied to the average thermal cracking unit, would be approximately as follows: The bubble tower bottoms would be recycled in the usual manner to the cracking coil and the heavy naphtha from crude fractionation can be injected into this stream ahead of the cracking coil charge pump. The clay slurry, containing approximately 20 lbs. of clay per barrel, would be introduced into the charge as it enters the furnace. To better control the linear velocity and the V/V/hr. in the coil, a small amount of water would be injected at the coil inlet.

The temperature and back pressure on the furnace would be adjusted to insure complete vaporization in the outlet stream, and it is estimated that the outlet temperature would be in the range of 1025-1050° F. and the back pressure 400-500 psi. The vapor stream from the furnace would be quenched with fresh feed, reduced crude, gas oil or cycle stock before passing into the evaporator. The reduced crude is used as quench at the outlet of the cracking coil. The quenched stream would pass through a venturi choke sized for the flow and conditions to serve as a release valve. The temperature and/or quantity of the quenching stream would be adjusted to maintain the proper temperature in the evaporator.



Special pumps for injecting catalyst slurry into the coils of the Suspensoid catalytic cracking unit at Sarnia. The gas compressor for pressure filters is in the right foreground

Uses Rotary Filter

The evaporator and bubble tower operations would be the same as for thermal cracking; the fuel oil that is removed from the evaporator would be stripped of light ends and cooled to approximately 500°. This fuel oil contains all of the clay injected into the cracking coil charge and this slurry is filtered by means of an Oliver Precoat rotary filter. The filtered fuel oil is of particularly high quality as all salts and carbon are removed along with the clay. The spent catalyst would be discharged

from the filter and discarded. This clay, being coated with low gravity fuel oil, makes fairly good fill and can be used for this purpose in low spots adjacent to the refinery.

The slurry makeup system is chiefly a slurry tank with agitator to which clay can be added, either directly into the tank or by means of a circulating pump and an eductor. The clay is slurried in cool cycle gas oil and it is this mixture that is pumped into the coil inlet. A special pump, made by National Transit especially for handling these slurries against very high pressures, is used to proportion the slurry to the cracking unit. The practice at the Sarnia refinery has indicated that approximately 2 lbs. of spent Super Filtrol from the lubricating oil clay contact plant per barrel of coil charge is sufficient for the desired effect.

More Active Than Spent Clay

Studies on the effect of varying amounts and types of catalyst have indicated that fresh Super Filtrol is more active than the spent lube clay, but not sufficiently greater to warrant its use as long as the spent clay is available. Spent Suspensoid catalyst has very little activity. Synthetic catalysts have a considerably greater activity than the Super Filtrol, it has been demonstrated on a pilot plant scale, but as noted previously, their costs make them impractical for the once-through operation. Two pounds of Super Filtrol per barrel of coil charge appears to be about the optimum in the Imperial operation at Sarnia, since increments of catalyst above this amount seem to have a relatively small effect. It should be possible to use blends of catalysts to achieve a balance of quality and economy and it is estimated that the catalyst cost in the Suspensoid operation will be between 4 and 5 cts. per bbl. of fresh feed.

Study Erosion Carefully

In the early development of the process, erosion in the coil and of the release valve was studied very carefully. At the Imperial refinery when the Suspensoid operation was carried out at the proper conditions of temperature and pressure, and with proper design, it was found that the erosion of headers and tubes in the furnace was very little greater, if any, than under thermal cracking conditions. As would be expected, lowering of the pressure in the coil can produce rather serious erosion since under these conditions the velocity would be considerably greater. If it is necessary to increase the temperature of the coil outlet, as was done at Imperial during the war in the Supersuspensoid operation to produce large quantities of butylenes, it becomes necessary to reduce the pressure on the coil to prevent coking. For this reason, the Supersuspensoid operation causes somewhat greater erosion, and special streamlined headers were used on the Imperial units to minimize this effect. The Imperial technologists believe that a unit can be designed to operate even at the lower pressures without excessive erosion.

The pressure release valve was a particularly serious erosion problem, but this was solved by the installation of a venturi choke inserted in the transfer line just as it ties into the evaporator. Thus, when flashed the mixture expands directly into the evaporator. In this manner, the clay does not travel through a restricted pipe section and thus cannot erode any metal except at the instant of passing through the orifice.

Other early problems were filter operation and slurry pump operation, but the difficulties have been eliminated in both cases by new developments in equipment and operating technique.

That data of Imperial Oil Ltd. on the operation of the thermal coils previous to the Suspensoid operation show that the yield of gasoline from Suspensoid is comparable to that obtained in thermal cracking and in the other catalytic methods. It is, of course, very difficult to compare yields or product qualities as these can be varied so widely, depending upon charging stocks and operating conditions. The product quality that Imperial has shown indicates an octane number above thermal of approximately 7-8 points on Motor method and 11-12 by the Research method. The lead susceptibility is slightly less with Suspensoid than with Thermal (approximately 10-15%), but better than with the Fluid catalytic cracking process. As would be expected, the fuel oil yield is considerably less and the gas yield considerably greater with Suspensoid than with Thermal. The increase in product volume is not quite as great as in the Fluid or TCC processes.

The yield of excess butylenes is higher than with thermal and a considerable additional improvement in yield and octane number can be obtained from Suspensoid in combination with a non-selective polymerization operation. On typical Mid-Continent stocks, a combined heavy naphtha-gas oil Suspensoid operation will produce a gasoline with a Research number of approximately 91-92 with 3 cc's of TEL. Including non-selective polymer, this Research octane number could probably be increased to 93-94. Where polymerization is practiced, a higher octane product can be produced without a decrease in gasoline yield by further increasing the conversion level to approach the Supersuspensoid operation. The fuel oil yield, however, is further reduced in this more severe operation.

Currently, the Research and Development Department of Imperial Oil Ltd., under the direction of Dr. R. K. Stratford, is continuing to study the Suspensoid process. A catalyst regeneration system is being developed and the effect of varying the quantity and activity of the catalyst is also being studied.

Not Equal to TCC or Fluid

The Suspensoid process, using small quantities of natural catalyst on a once-through basis, should not be considered the equivalent of the TCC or Fluid processes from the standpoint of product yield or quality, but the Suspensoid process does produce a good margin of improvement over thermal cracking at a cost considerably less than the other catalytic methods. It has been estimated that the additional operating costs above thermal cracking will be less than 12c barrel of fresh feed and savings in TEL requirements alone should more than cover this increased cost. These facts coupled with the simplicity and flexibility of the process should make it particularly attractive for the small refiner.

The Standard Oil Development Co. is prepared to grant licenses under its patents on the Suspensoid catalytic cracking process at reasonable terms.

General view of catalyst slurry and fuel oil filtration building. Fresh catalyst hoppers are at upper left

TOMORROW

...IN PETROLEUM TECHNOLOGY

Current technological and economic developments discussed here in the light of their future bearing on petroleum refining operations include:

- **Radiation chemistry offers intriguing prospects.**
- **Greater capital expenditures trouble economists.**
- **Naphthenic acids find wide commercial usage.**
- **Vinyls need growing quantities of petroleum materials.**

Radiation Chemistry Offers Intriguing Prospects

IT IS not surprising, considering the secrecy which enshrouds everything connected with nuclear energy, that very little has been published concerning its potential role in petroleum processing operations. Not that this role has gone unnoticed, however; it would be safe to wager that most large petroleum research organizations have chemists and physicists busily engaged in preliminary studies. Moreover, somewhat unauthenticated reports of radioactive catalytic cracking have appeared from time to time.

It is more than interesting to note, then, that several brief glimpses of future uses are given in a booklet of "scientific information transmitted to the United Nations Atomic Energy Commission."(1) According to Arthur H. Compton and Zay Jeffries, authors of a chapter on the "Future of Atomic Energy," radioactive atoms of a given element may be used as tracers to answer "questions as to how, and how fast, atoms transfer from one molecule to another or from one place to another in the course of a chemical process, including such processes as corrosion, diffusion, adsorption of molecules on surfaces, and formation and destruction of colloids.

"The use of radioactive tracer atoms holds much promise for the study of the composition of liquids and vapors in equilibrium with each other, and for studying the performance of distillation columns and other equipment used in chemical engineering, *for example, in the oil industry.* Particularly important as a tracer in the oil industry and wherever carbon compounds are concerned will be the carbon isotope C-14.

"The radiations from the fission chain reaction are capable of inducing chemical reactions which cannot ordinarily be carried out, since one effect of radiation is a sort of catalysis of thermodynamically possible reactions."

This subject is further elaborated upon in a chapter on "Practical Applications of Radium Chemistry" by James Franck and Milton Burton, who point out that "the high-energy radiations now available for radiation chemistry (alpha and beta particles, fast neutrons, fission recoils, and gamma rays) are very penetrating, thus permitting treatment of large quantities of materials. All substances treated by such radiations can be profoundly affected. However, the penetration is accompanied by a loss of specificity; often a host of substances, useful and useless alike, are produced simultaneously. This is somewhat compensated by the high intensity of radiation fields available for such work . . . Studies of complicated organic substances indicate that, under certain conditions, the disadvantage of nonspecificity of high-energy radiation can be avoided, so that only a few substances are preferentially produced. . . .

"We may anticipate economic advantages (of the application of radiation chemistry) in the vast field of polymerization processes which are now so successfully applied in the manufacture of plastics, rubber, etc.; in this field, in fact, initial successes have already been obtained. In a similar connection, studies even prior to the war on the effects of radiation on some of the constituents of natural gas indicate that they may be converted, via the medium of radiation chemistry, into industrially important products. Their present uses (e. g., in the production of carbon black or for fuel) are economically unsound(?).

"Related to such processes in a certain sense is the low-temperature cracking of oils, which should be intensively studied. Radiation chemistry here presents the opportunity of a new technique which may produce new and very interesting products."

The present "socialization" of atomic (nuclear) energy and its uses, through Government control, makes it difficult to predict how and when such processes will be applied. Nevertheless, it seems highly probable that petroleum processing, which has just passed from the "thermal" to the "catalytic" stage, is about to enter into the "atomic" period.

Greater Capital Expenditures Trouble Economists

IN THE evaluation of any process, be it catalytic cracking or Synthine synthesis, the investment required is always an important criterion, second only to the final cost of the product, amortization included. This capital must either be raised or allocated; in either case, comparable returns from other applications must be considered, along with the risk of premature obsolescence.

In the petroleum industry, the struggle to provide better and better products at lower costs has been possible "only through larger and larger capital expenditures, and future advances will require still more expensive equipment. Based on 1947 construction costs, the investment required per barrel per day of product has risen as follows, with increases in the complexity of the operations:(2)

TABLE 1—Rise in Investment Costs per Daily Barrel of Product in the Petroleum Industry

	Costs per Daily Barrel	
Operation	**1939**	**1947**
Skimming	$180	$300
Topping and thermal cracking	600	1,000
Topping and catalytic cracking	900	1,500
Synthetic oil from natural gas	2,100	3,500
Synthetic oil from coal	3,000	5,500

"The use of capital for this necessary equipment and for the higher costs of finding oil should not be discouraged by Government policies which prevent an adequate return on the investment required. Given the right environment, the petroleum industry feels confident that it can maintain the country's supply of vitally necessary liquid fuels and lubri-

(1) Tolman, R. C. (Ed.), *The International Control of Atomic Energy*, Department of State Publication 2661 (The United States and The United Nation Report Series 5), Superintendent of Documents (Washington), 1947. 195 pages. 30 cents.

(2) Wilson, R. E. and Roberts, J. K., "Petroleum and Natural Gas—Uses and Possible Replacements." Paper presented at Western Petroleum Refiners Association 35th Annual Meeting, March 24-26, 1947.

cants at reasonable costs for many generations to come."[2]

The petroleum industry is not alone in its concern with rising investment requirements. As pointed out by R. A. Kinckner of du Pont,[3] "rising construction costs present a serious problem to the chemical industry. Many installations which would have shown an adequate return on the investment in the prewar period present a different picture in the light of the greatly increased costs of construction which prevail today."

Five means of minimizing investments are cited: (1) Elimination of over-design, (2) use of continuous processing, (3) use of control instruments to maintain capacity at a maximum, (4) use of proper materials of construction, and (5) development and use of efficient types of equipment. . . . Construction costs have risen 75% over prewar levels, and this trend may continue. Returns are being further diminished by the high levels of Federal taxes. The return of competitive markets will seriously jeopardize excessive investment."[3]

No chemical engineering branch is more active in continual plant construction than is the petroleum processing industry, hence no industry is more concerned with the rise in the cost of construction and equipment. It is very evident, from the table presented by Wilson and Roberts,[2] that the published economic data of the past must be adjusted upward if they are to have present validity, and it is equally evident that all data past and present—must be carefully scrutinized before major plant constructions are begun.

Naphthenic Acids Find Wide Commercial Usage

DURING the past year, the Bureau of the Census has been engaged, in its "Facts for Industry" series, in releasing statistics which show the "wartime end-use pattern" for various chemicals which played important or secondary roles in the war program. Many of these brief reports deal with petroleum by-products and derivatives, and a recent one, concerned with naphthenic acid,[4] contains some figures which might be of particular interest because 77.3% of usage was other than "direct military"; i. e., the normal use pattern is more clear.

As stated in this release, "naphthenic acid comprises the monobasic carboxylic acids that exist naturally in crude petroleum and its distillates, RCOOH, when R is the naphthene radical. The term also includes the sodium salts of these acids when used to prepare metallic naphthenates. For most of the end uses listed (in this release), the acid was used after conversion to a naphthenate other than sodium naphthenate. . . . The data represent wartime distribution, with allocations permitted only for identifiable military uses and other essential requirements."

For the 12-month period July 1, 1944-June 30, 1945, total allocations of naphthenic acid amounted to 31,761,000 pounds, of which 7,220,000 pounds were used for "direct military" purposes, 2,000 pounds were exported and 24,539,000 pounds went to the following "other uses":

TABLE 2—Civilian Uses of Napthenic Acid for period July 1, 1944 to June 30, 1945 (excludes military and exports)

Uses	Pounds
Fungicides and wood preservatives	15,619,000
Driers	4,911,000
High-pressure lubricants	1,319,000
Rust preventatives	961,000
Ore flotation, solvation, emulsification	804,000
Cutting oils	405,000
Metal cleaning and degreasing	161,000
Miscellaneous uses and small orders	359,000
Total	24,539,000

It is no secret that the "direct military" uses of the naphthenates included the manufacture of sandbags, tents, tarpaulins, jungle clothing, awnings, sail cloth, cordage for camouflage nets, etc., for the copper naphthenates are powerful fungicides for mildewproofing; other military uses were concerned with wood preservation. In addition to the civilian uses listed in the table (or, in some cases, as further subdivisions of these), applications also include printing ink solvents, cotton sizing, emulsifying agents, spray oil emulsions, waterproofing agents, wetting agents, and rubber compounding agents.

Wartime allocations are no fair picture of peacetime distribution, where relative demands are different and military necessity is no factor. Nevertheless, it is not often that such a complete picture of uses for a specific chemical becomes available.

Vinyls Need Growing Quantities Of Petroleum Materials

A RECENT article on "Vinyl Resins as Consumers of C_2H_2 and C_2H_4"[5] is of some little interest as a source of pertinent statistics on a group of resins which has recently assumed imposing stature in the plastics field. These resins, derived either from acetylene or ethylene, are of definite interest to the petroleum industry which produces large quantities of the latter chemical and is at least potentially a fruitful source of the former.

Vinyl acetate resins, according to this article, require (for the present method involving acetylene and acetic acid) approximately 340 pounds of acetylene and 780 pounds of acetic acid per 1,000 pounds of polymer; if the acetic acid is also derived from acetylene, total requirements for the latter become 775 pounds.

Vinyl chloride resins, if based on the dichlorination of ethylene followed by dehydrochlorination, require 470 pounds of ethylene and 1,200 pounds of chlorine per 1,000 pounds of resin. If acetylene and hydrogen chloride are the raw materials, 450 and 640 pounds are respectively required to produce 1,000 pounds of resin.

For the other vinyl resins, the following are typical requirements per 1,000 pounds of resins: (1) Vinyl chloride-vinyl acetate copolymers—varying combinations of the above, with the percentage of vinyl chloride usually 80-95%; (2) vinylidene chloride polymers—375 pounds of ethylene and 1,760 pounds of chlorine; (3) polyvinyl alcohol (90% hydrolyzed)—1,800 pounds of polyvinyl acetate and 790 pounds of methanol); and (4) polyvinyl butyral (70% aldehyde content), 650 pounds of polyvinyl acetate and 400 pounds of butyraldehyde.

The significance of these figures is clearer when it is noted that 70,000,000 pounds of acetylene and ethylene (on an acetylene basis and including a factor for acetic acid), 49,000,000 pounds of hydrogen chloride and chlorine, 5,500,000-6,000,000 pounds of aldehydes, and 7,000,000 pounds of methanol were required for the 1944 production of the vinyl resins. In that year, about 85,000,000 pounds of vinyl chloride (and copolymer) resins were produced, along with 15,000,000 pounds of polyvinyl acetals (chiefly the butyral), 3,000,000 pounds of polyvinyl alcohol, etc.

Production has continued to increase, 1945 vinyl resin production totaled 122,000,000 pounds; 1946 production amounted to 145,000,000 pounds; and 1947 production may approach 200,000,000 pounds, depending on the availability of plasticizers (chiefly phthalic anhydride esters).

If one were to carry the calculations of basic materials back still farther, it would be easily possible to estimate the amounts of petroleum chemical fractions which went into some of the other intermediates mentioned above, for methanol and butyraldehyde are also producible from these materials. In any case, it is clearly evident that these resins are already providing quantity markets (as chemicals go) for certain present and potential "chemicals from petroleum" (i. e., the basic materials for these), and it is equally pertinent to note, elsewhere, that the potential demand for these resins is probably considerably more than twice the 1947 estimate.

(3) Kinckner, R. A., *Chemical Engineering Progress* 43, No. 4, 183 (1947), "Investments and the Engineer."

(4) Anon., *Naphthenic Acid in the War Program*, Department of Commerce, Bureau of the Census "Facts for Industry" Series 6-8-51, Washington, 1947.

(5) Atlas, H. H. and Aries, Robert S., *Chemical Engineering* 54, No. 3, 101 (1947), "Vinyl Resins as Consumers of C_2H_2 and C_2H_4."

This article below, exclusive in PETROLEUM PROCESSING, is the first to be published describing the design details of Mexico's improved refinery installations at Atzcapotzalco

Product Flexibility, Low Fuel Consumption Feature Modernized Pemex Refinery

By RAFAEL ORTIZ MENA, Petroleos Mexicanos
and
S. A. GUERRIERI and D. W. WILSON, Arthur G. McKee & Co.

New processing units have been installed and existing units modernized at the Atzcapotzalco refinery of Petroleos Mexicanos near Mexico City, as part of the coordinated expansion of the petroleum facilities in the central part of Mexico.

While started as a wartime project to provide primarily aviation gasoline, plant design and engineering provided flexibility to meet later peacetime requirements, particularly for such fuel products as fuel oil, stove distillate and liquefied petroleum gas. The refinery's crude charging capacity has been increased from 20,000 to nearly 50,000 b/d.

Plant additions at Pemex include a new crude distillation unit, straight-run fractionation and treating equipment, thermal cracking facilities, butane isomerization unit and HF alkylation unit. Existing crude distillation units were modernized and additions made to the miscellaneous utility and service facilities.

Extensive use has been made of reflux operations and heat exchangers for maximum heat recovery and minimum consumption of fuel. Extensive filtration facilities are employed to remove water during process flow so as to control corrosion due to the relatively high percentages of hydrogen sulfide present. The refinery is largely motor driven and includes the equipment to provide all its own power.

NEW PRODUCTION and refining facilities now being completed in the central part of Mexico, although planned and started as a wartime project, will be equally important in serving that country's peacetime needs for petroleum products. In fact, they are essential to her continued progress and healthy economy.

Included in the project are:

1. Crude oil and gas gathering lines, crude oil desalting and stabilizing installations, gas absorption units, and auxiliary power, water, and service facilities in the Poza Rica oil fields.

2. Improvements and increases in capacity in the 150-mile pipe line system connecting the Poza Rica field and the Atzcapotzalco refinery, 8 miles from Mexico City.

3. New installations together with revamping of existing units to increase the capacity and scope of operations of the Atzcapotzalco refinery.

The new crude unit at the refinery has been operating several months well beyond design capacity. The thermal cracking unit has been on stream for some time, as has been the boiler plant, power generation, water system, and miscellaneous facilities. Balance of processing units are expected to be in full operation by the middle of July, 1947.

The location of these new production and refining facilities with respect to the rest of Mexico is shown in the map of the country, Fig. 1.

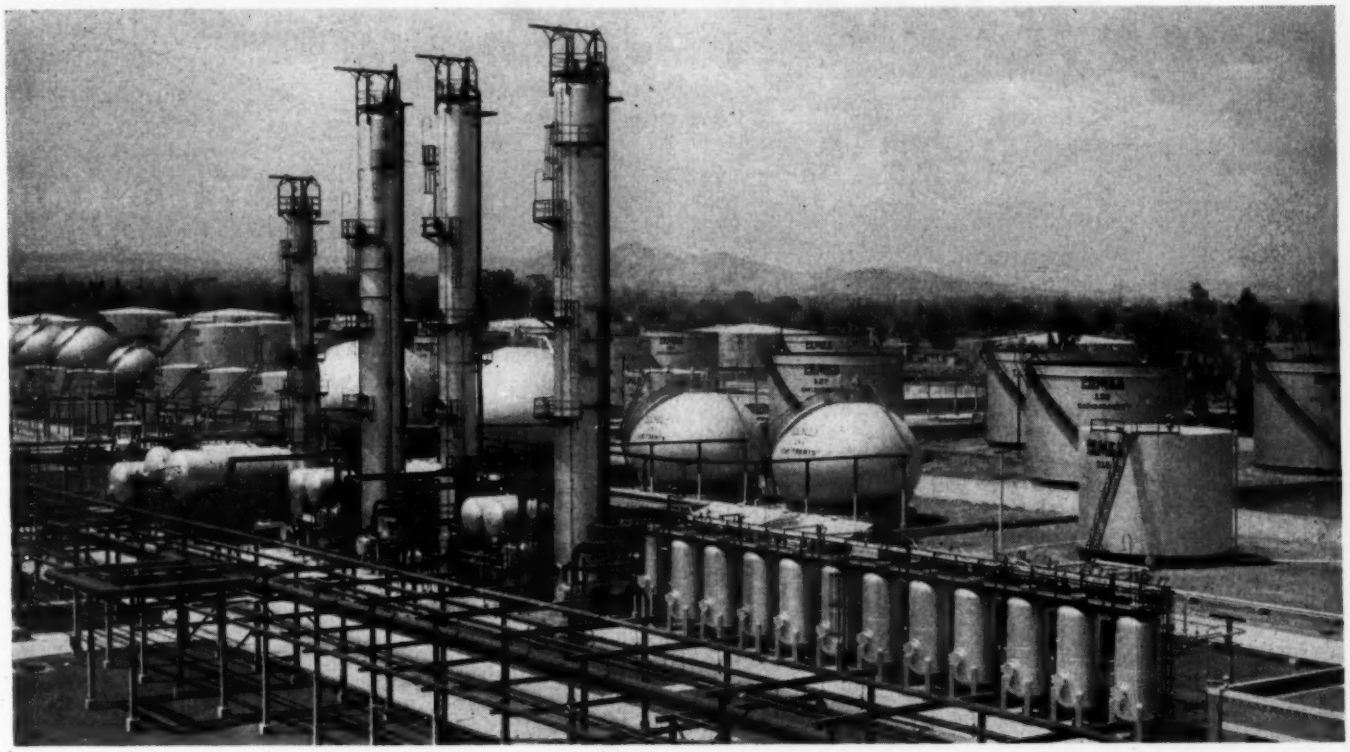
The entire project was formulated on the basis of producing 1000 b/d of aviation gasoline and accompanying essential commercial products. The stringent shortages of construction materials when it was initiated during World War II, however, sharply limited the scope of the work. Sufficient construction materials could not be obtained for all the facilities necessary to supply all the petroleum needs in the central zone of the Republic, served by the Atzcapotzalco refinery.

Shortage Would Increase

Without the addition of the new facilities there would now be an increasing shortage of all kinds of petroleum products in the central area of the country, and as a result transportation and industry would necessarily stagnate. Even with them, however, there will continue to a need, beyond the capacity of the new equipment, for fuel oils for railroad and industrial operations. Furthermore, certain products such as paraffin waxes and lubricants, which are in short supply in this area, cannot now be produced at the Atzcapotzalco refinery. Circumstances with respect to construction materials did not permit including facilities for their manufacture in the project.

The coordinated expansion of Mexico's petroleum facilities is being handled by Petroleos Mexicanos, the petroleum agency of the Mexican Government. This agency is now headed by and under the direction of Senator Antonio J. Bermudez, although the program discussed in this paper was planned by Efrain Buenrostro, until recently General Manager of Petroleos Mexicanos, and some of his assistants. In view of its initiation during World War II, the proposition was carefully reviewed and examined by several agencies of the United States Government, in particular the Petroleum Administration for War.

More than one-half of the estimated $24,000,000 cost of this whole project was financed by Petroleos Mexicanos. $10,000,000 for the purchase of United States materials was made available by means of a loan from the United States Export Import Bank. Of this loan it is interesting to note that more than $2,-



Photos Courtesy Arthur G. McKee & Co. and Petroleos Mexicanos

General view of portion of Pemex refinery at Atzcapotzalco. Isobutane and isopentane towers in foreground, bank of copper treaters at the right

000,000 has already been repaid by Petroleos Mexicanos.

The design, engineering, purchasing, construction, and similar services were handled by Arthur G. McKee & Co. Mexican engineers familiar with United States practices are in charge of operation of the various units, and Phillips Petroleum Co. has been acting as supervisor for the Export Import Bank throughout the project and is still functioning in this capacity during the initial operating period.

The modifications in the crude oil pipe line will not be discussed in detail in this paper, but it may be well at this point to mention that the existing 10-in. pipe line from the producing area on the coast to the refinery will be used with minor looping only. The crude oil pipe line is approximately 150 miles long, and in this distance it rises over very rugged country from sea level to a maximum elevation of about 8500 ft.

The previously existing oil pumping facilities consisted of six stations, each equipped with motor driven reciprocating pumps. The modifications include the addition at each of these stations of motor driven centrifugal pumps and the further addition of three completely new pumping stations. The more complete description of the problems encountered in modifying and enlarging this line capacity includes many interesting features but the scope of this paper does not contemplate inclusion of such discussion.

The new facilities at the Poza Rica oil fields include a new absorption unit to handle all the gas produced in this field, crude desalting equipment, a crude stabilization unit, hydrogen sulfide purification for compressor fuel only, the necessary gas and oil gathering lines and facilities, and auxiliary equipment and services such as tankage, electricity, water supply, laboratory equipment, and the like.

Since the purpose of this paper is primarily the discussion of the modified and enlarged refining facilities at the Atzcapotzalco refinery it will not be

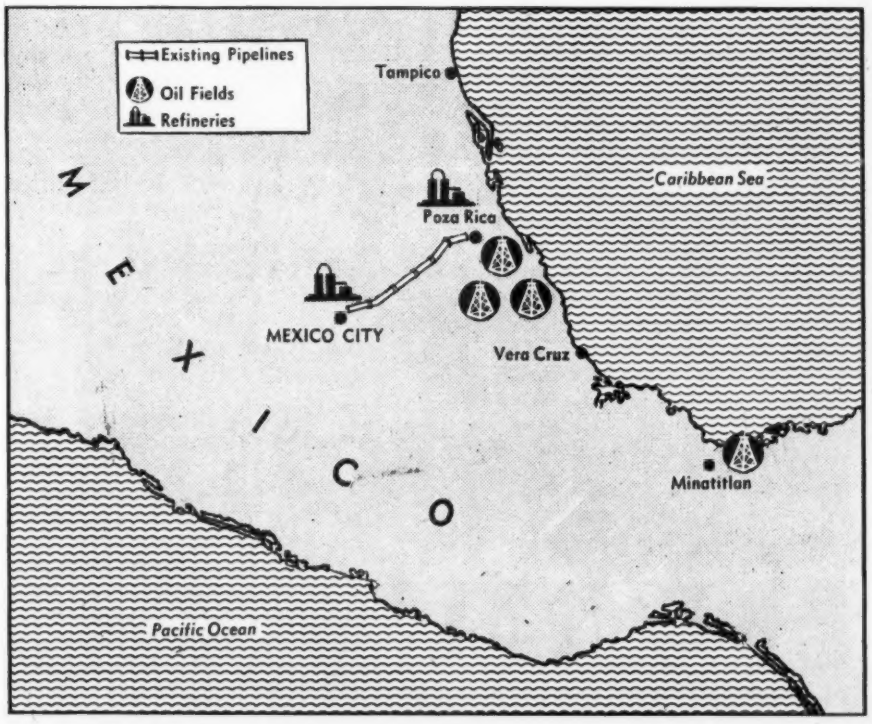
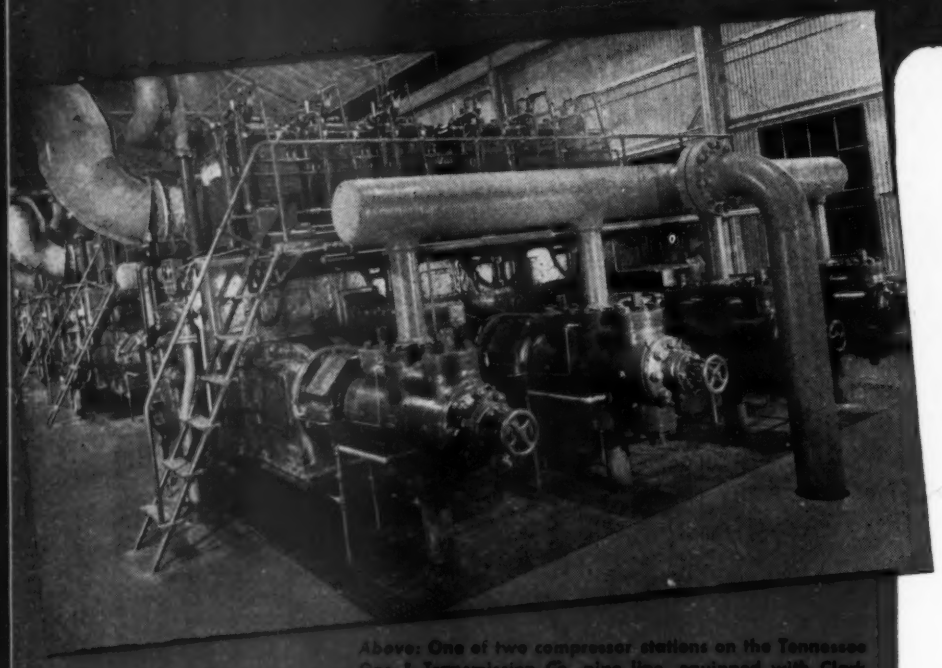


Fig. 1—Map shows relationship of Mexico City refinery, Poza Rica facilities, and pipeline to other major oil centers

GAS PIPE LINES
HAVE CHOSEN

400,000 BHP of Clark Compressors

IN LAST TEN YEARS



Above: One of two compressor stations on the Tennessee Gas & Transmission Co. pipe line, equipped with Clark "Big Angle" gas-engine-driven compressors. Each installation consists of nine 6-cyl., 1,200 BHP units.

Below: At Jal, New Mexico, on El Paso Natural Gas Co. pipe line, installation consists of 8 Clark 8-cyl. Right Angle Compressors, a total of 6,400 BHP.

● The roll call of great pipe lines using Clark engine-compressors includes the following partial list of famous names:

Colorado Interstate Gas Co.
Consumers Power Co.
East Ohio Gas Co.
El Paso Natural Gas Co.
Hope Natural Gas Co.
Memphis Natural Gas Co.
New York State Natural Gas Co.
Panhandle Eastern Pipe Line Co.
Southern Union Gas Co.
Tennessee Gas & Transmission Co.

The proved performance of Clark units in this service is indicated by the impressive 10-year total of 400,000 BHP either in use or now in production, for gas pipe line stations exclusively.

More than one third of that total, or 145,200 BHP, consists of "Big Angle" Compressors, the first unit of which was placed in service 4½ years ago.

Rating 200 BHP per cylinder, the Clark "Big Angle" is the most powerful right angle gas-engine-driven compressor ever built. It is the answer to the need for *greater power in less space* and at *lower over-all cost.* Sizes: 5-cyl. 1,000 BHP; 6-cyl. 1,200 BHP; 8-cyl. 1,600 BHP; 10-cyl. 2,000 BHP.

CLARK BROS. CO., INC.,
Olean, New York

Boston • Chicago • Houston • Los Angeles
New York • Tulsa • Washington • London
Bucharest, Roumania • Caracas, Venezuela

CLARK

ONE OF THE DRESSER INDUSTRIES

SETS THE PACE IN
COMPRESSOR PROGRESS

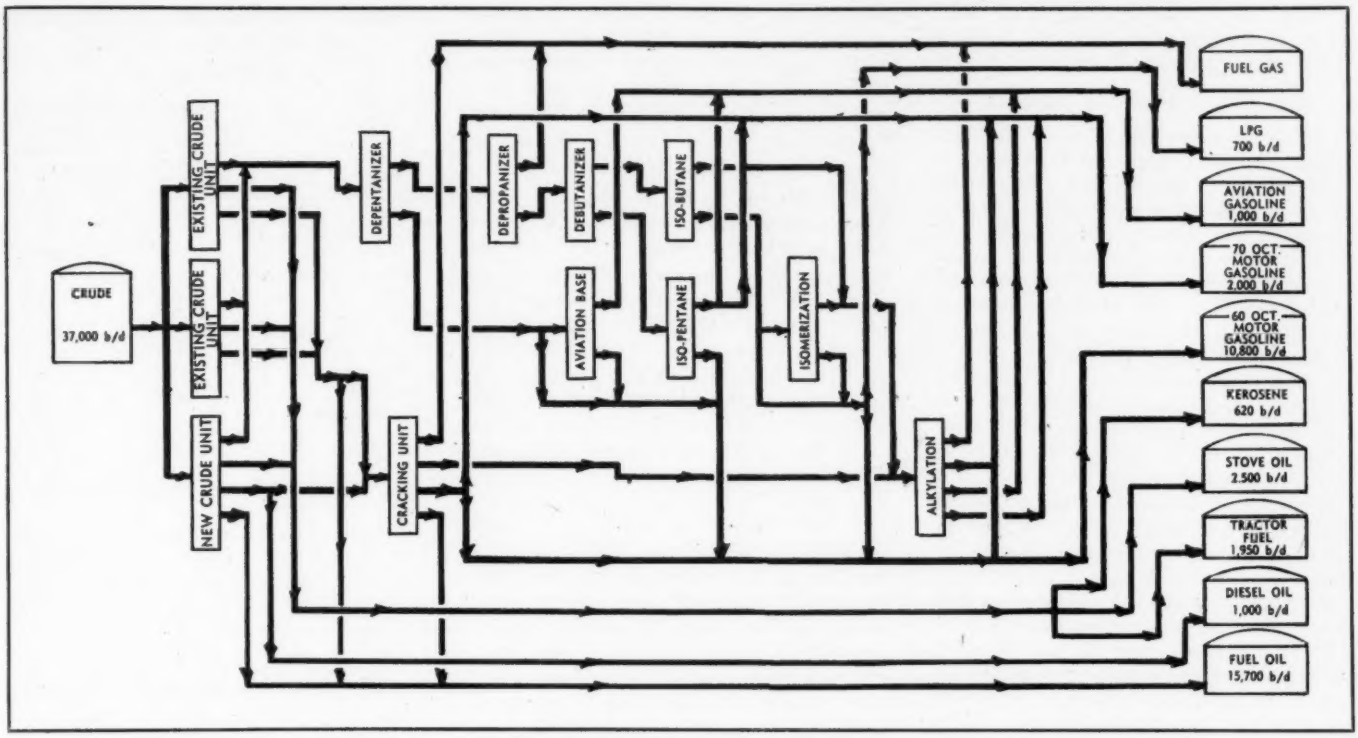


Fig. 2—General flow diagram of Atzcapotzalco refinery. Figures are based on design conditions and are in barrels per calendar day

attempted to discuss at any length the Poza Rica field facilities. However, it seems of interest to mention briefly some of the outstanding features with respect to these operations in the field.

Oil Field is 150 Miles Away

The Poza Rica field is located about 150 miles northeast of Mexico City and about 35 miles southwest of the Port of Tuxpan in the Mexican Gulf. This field is entirely owned and controlled by Petroleos Mexicanos and consequently it is possible to maintain completely unitary operations in the field. Production practices generally are excellent. Meters and individual separators permit the measurement of gas and oil from each well. The terrain at Poza Rica is irregular and hilly, and gas separation batteries have been so located that maximum advantage is taken of gravity flow.

The new processing facilities at Poza Rica are grouped in a central location and oil and gas are brought to this plant from four outlying locations. From each of these outlying areas one 400 psi gas line and one 60 psi line convey gas to the new central processing area. Atmospheric vapors are compressed at the outlying separator stations to 60 psi and pass into this intermediate pressure line. From each outlying location there are also two independent oil lines. The salt content of the oil varies from well to well and it is both useful and practical to separate the oil as produced into high salt crude requiring later desalting and low salt crude which bypasses the desalting unit.

The basis for the design of the new facilities at Poza Rica has been the production of 65,000 bbls. of oil and 75,000,000 cu ft of gas per calendar day.

Consideration during the design was given to the major facilities which might later be required in the case of higher production. The absorption plant is expected to operate for the immediate future at 300 psi but a future operation at 600 psi has been considered and substantially all of the major equipment is capable of operating at this condition. By this means maximum economic provisions have been made now for future increased production at the Poza Rica field and a minimum of later additions will be required.

Refinery Capacity Up 100%

The design crude capacity of the refinery at Atzcapotzalco contemplated an increase of about 100%, from 20,000 to 40,000 b/d, by a number of major improvements. Early actual operating results indicate that 50,000 b/d may be processed. The new facilities include:

1. A new crude distillation unit.
2. Changes to the two existing crude distillation units.
3. Straightrun products fractionation equipment.
4. Light straightrun products treating.
5. Thermal cracking facilities.
6. Treating of cracked stocks.
7. Butane isomerization unit.
8. HF alkylation unit.
9. Boilers and power generation equipment.
10. Water supply system.
11. Atmospheric and pressure storage.
12. Miscellaneous facilities such as transfer pumping, yard piping, lighting, wiring, tetraethyl lead blending plant, new laboratory, and similar necessary auxiliaries.

Before discussing somewhat more completely the various refinery units itemized above, certain general observations as to petroleum and its place and needs in Mexico should be made, for these factors greatly influenced the design of the refinery.

Transportation Depends on Oil

It should be emphasized first that there are no known substantial coal resources in the country. It is therefore necessary that railroads, trucks, and other transportation means, as well as industries, shall meet their fuel demands largely by the use of residual oils from petroleum.

As in many other Latin American countries, transportation is a pressing problem within Mexico and this need is being met and must continue to be met by the expansion of highway, railroad, and airplane facilities. The motive power for these transportation needs, and for industrial purposes, must necessarily be supplied from petroleum. These conditions then create a present and probable future situation in Mexico with large and increasing requirements for residual fuel oils.

It is desired to emphasize this situation since it is at variance with conditions prevailing for the most part in the U. S. It will be recalled that Petroleos Mexicanos is an agency of the Government of Mexico and consequently most careful attention must be paid to the inherent needs of the country, even though price structures for petroleum products might not always indicate that the maximum

income may be derived from such relatively large production of residual fuels as are needed in Mexico.

High Octane Fuel Not Necessary

Referring now generally to the facilities at the Atzcapotzalco refinery, it is of interest to observe that substantially all of the gasoline expected to be produced in this refinery will be consumed in the Mexico City region, all of which lies at an elevation of 7500 ft above sea level, or higher. This altitude minimizes the inherent need for gasoline of as high octane as is presently being considered in the U. S. Fuel rated at 60 motor method octane compares in performance with 72-75 octane when considering the elevation of Mexico City as compared to sea level.

With further reference to the expanded Atzcapotzalco refinery, it must be remembered that this entire project was initiated in the midst of war and that a primary consideration in its planning was the production of approximately 1000 b/d of top grade aviation gasoline and those attendant essential commercial petroleum products needed to maintain the economy of Mexico. In any study of this project these underlying factors must always be borne in mind since they determined the scope of the work in nearly all respects.

An extensive investigation was made with respect to the required light ends, especially butanes and butylenes, for the aviation gasoline manufacture. After study of all available information, the conclusion was reached that the isobutane available from natural sources at the Poza Rica oil field could not safely be relied upon to satisfy the demands for the required alkylate. On this basis it was deemed necessary to provide a butane isomerization unit at Mexico City. Fortunately, the availability of normal butane from natural sources was such as to make this practical after due allowance for the butane requirements for motor gasoline and other purposes. The thermal cracking unit, as will be developed more fully later, is of a capacity which will provide unsaturated feed stock for alkylation consisting chiefly of butylenes but with an appreciable and variable amylene content in the charge to the alkylation unit.

The petroleum products presently produced and those contemplated after completion of the additions to the Atzcapotzalco refinery are shown in Table 1. General Flow is in Fig. 2.

The figures given in Table 1 have been approximated somewhat and are not sufficiently exact and definite to permit material balances as compared with crude oil charge capacity and other figures given elsewhere in this report. The quantities given in the second column of the table are those corresponding to the design basis for the refinery and contain inherently the safety factors ordinarily employed in good practice for such design. The terms "100 octane", "70 octane", and "60 octane" are used to indicate respectively the highest quality aviation gasoline as considered at the time the project was designed, a premium quality motor gasoline, and an ordinary grade housebrand motor gasoline. Kerosine, stove distillate, and tractor fuel differ very slightly in specifications and to a considerable extent production may be distributed at will between these three products.

Other Fuels Also Important

It is important at this point to mention that kerosine and stove distillate are especially essential in the Mexico City area since the city has no gas system or gas available at this time and, as has been mentioned, coal is practically non-existent in the country; wood—although available — is becoming increasingly scarce and its use for household purposes is being officially discouraged. Liquefied gas shown in Table 1 is not now produced at the Atzcapotzalco refinery and only a small quantity is contemplated from the new facilities. The importance of this to the economy of the central area of Mexico is self-evident in view of the absence, as just mentioned, of other suitable fuels.

It will be noted from Table 1 that petroleum products, after the present additions go into operation, are slightly more than double those produced from the previous operations. Even so it is estimated that the central area of Mexico will not be adequately supplied by products when those larger quantities are available.

TABLE 1 — Production Atzcapotzalco Refinery Before and After Modernization

	Barrels per Calendar Day Design Conditions	
	Before	After
100 octane aviation gasoline	.....	1000
70 octane motor gasoline	.....	2000
60 octane motor gasoline	5870	10,800
Kerosine	230	620
Stove distillate	.....	2500
Tractor fuel	710	1950
Diesel fuel	380	1000
Fuel oil	10,420	15,700
Liquefied gas	.....	700
Total	17,610	36,270

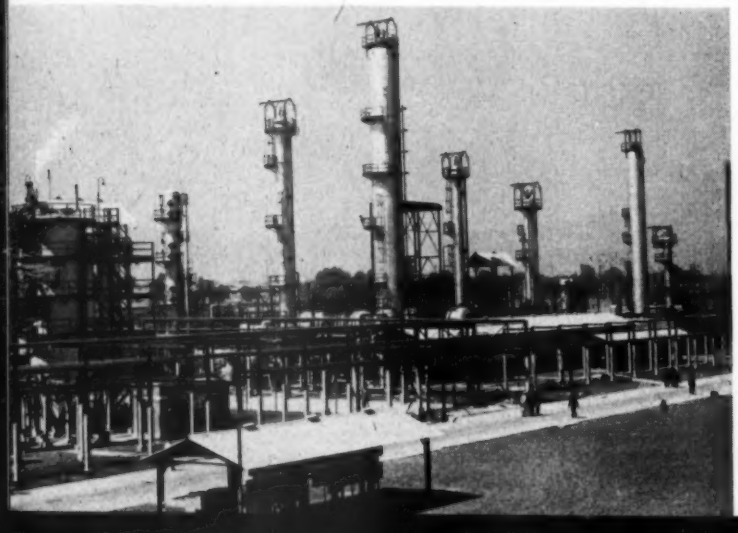
Attention is called to the fact that neither in the present facilities nor in those now being added is there any equipment for the production of lubricants or waxes. War conditions prevented including such facilities, although they were then and are now badly needed for this highly populous section of Mexico. The general design of the refinery, both from the standpoint of processing and of layout, has attempted to take into account future addition of wax and lubricant manufacturing units.

It is readily evident from Table 1 that the ratio of aviation gasoline produced to total crude run is very low when compared to many other plant designs. This was realized throughout all planning stages of the project and is due to the necessity for combining aviation gasoline production with the minimum required quantities of accompanying essential civilian products.

New Crude Distillation Unit

The existing plant at Atzcapotzalco included two crude oil topping units with a total crude oil processing capacity of about 17,000 b/d. (In this discussion all rates will refer to calendar days and, in the case of new or modified equipment, to the design capacity.) To increase plant thruput to the projected 37,000 b/d, a new 20,000 b/d crude unit has been installed and the existing units have been modified. The approximate charge and yield of products as designed are given in Table 2. The flow through the new crude oil distillation unit is given in Fig. 3.

This figure also includes the flow through the naphtha depentanizer and aviation base stock tower. In view of the fact that the process can readily be traced in this and other flow diagrams which follow, it is intended not to describe the process in detail, but rather



General view showing alkylation unit at left and isomerization unit at right

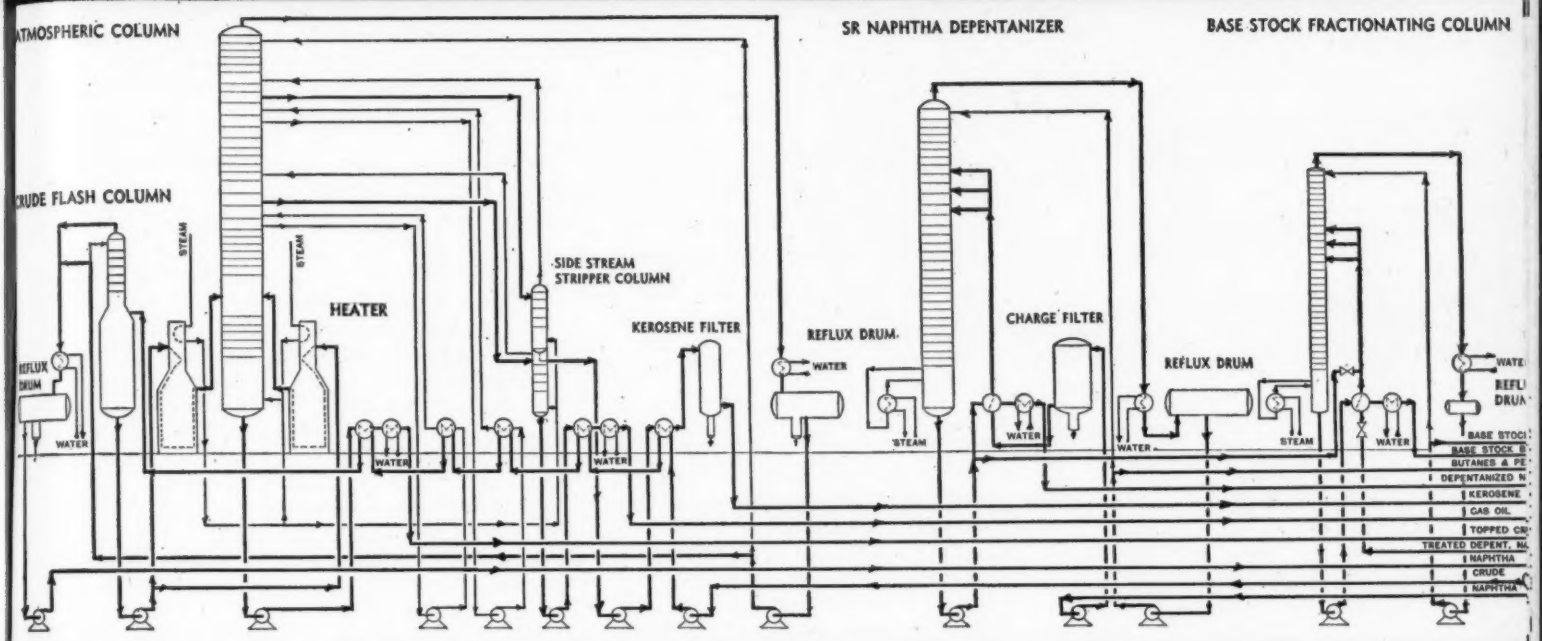


Fig. 3—Simplified flow diagram for the new crude distillation unit

to give the salient features of the design. There are a number of features of design of the crude oil distillation unit which may be of interest.

In the first place, it must be remembered that the elevation of the plant is some 7,700 feet above sea level. At this altitude atmospheric pressure is 11.2 psia instead of 14.7 psia, and hence the atmospheric boiling points are considerably lower than at sea level. Thus, the condensation of the lighter hydrocarbons under atmospheric pressure becomes somewhat more of a problem than at the lower altitudes.

In the second place, it is anticipated that the crude delivered to Atzcapotzalco will be stabilized and enriched at Poza Rica with all of the natural gasoline recovered there, and therefore will contain considerably more butanes and pentanes than is customarily found in natural crude oil. Naphtha produced from this crude would have a vapor pressure of about 15-18 psia; therefore, if it is produced as an overhead product from an atmospheric tower, complete condensation would be impossible.

On the other hand, operation of a crude oil distillation tower at a sufficient pressure to condense completely the butane-enriched naphtha was not desirable due to the fact that a flash temperature in excess of 600° F. would have been required. Such temperature would have been detrimental to the process for several reasons.

In the first place, there was a strong possibility that kerosine would have been thrown off-color by a higher feed temperature. In the second place, there was fair evidence to indicate that rather severe decomposition of the higher organic sulfides would take place above 600° F., thereby increasing the chances of corrosion of the equipment. This is, of course, aggravated by the introduction of stripping steam in the bottom of the column and sidestream strippers. Finally, additional heat would be required to process the crude in a single flash unit. This heat could only come from the combustion of additional fuel oil, which was already a scarce item in Mexico.

In view of these conditions it was decided to employ a flash column ahead of the main distillation column which would be operated dry and serve to remove a considerable fraction of the butanes and other lighter hydrocarbons in the crude. It was decided to operate this tower dry in order to minimize corrosion, since most of the hydrogen sulfide brought to the refinery in the crude would come out at this point. If the hydrogen sulfide could be kept dry corrosion would be very much reduced.

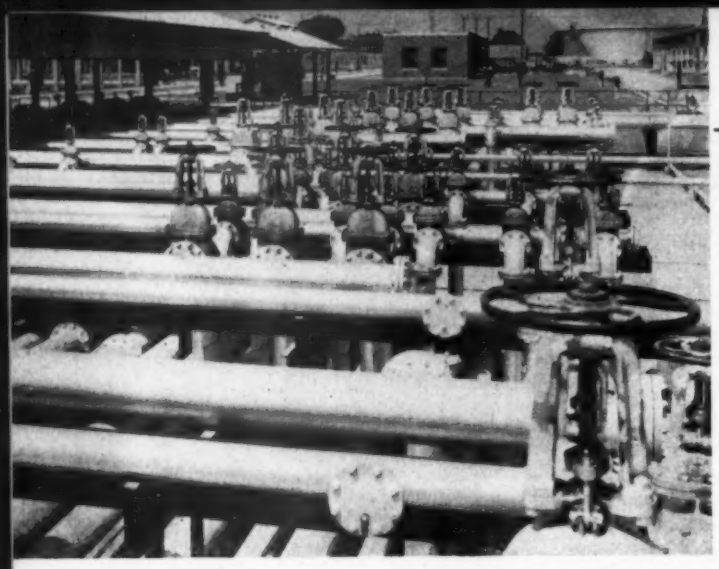
It also seemed desirable to operate this flash tower on exchange heat only. With this limitation it became desirable to operate the flash tower at as low a pressure as possible consistent with the requirement of complete condensation of the overhead.

In order to accomplish this purpose overhead naphtha recovered from the atmospheric tower is introduced into the vapor line of the overhead from the flash tower to assist in the condensation of the flash tower overhead. Under these conditions the flash tower may be operated at about 30 psia and complete condensation of overhead takes place. Since the fractionation of the overhead product from the flash tower is not a serious problem, the atmospheric tower naphtha is used for reflux here in only sufficient amount to assure proper end point of the flash tower overhead.

The principal feature in connection

TABLE 2—Crude Distillation Units—Feed and Products—Design Conditions

	New Unit		Modified Existing Units		TOTAL
	B/CD	API	B/CD	API	B/CD
Charge:					
Poza Rica Crude (Stabilized and butane enriched)	20,000	33-35	17,000	33-35	37,000
Products:					
Naphtha (Undepentanized)	5400	70-72	4590	70-72	9990
Kerosine distillate (1)	2740	44-46	2330	44-46	5070
Gas oil (2)	2390	33-35	.....	....	2390
Bottoms (3)	9470	16-18	10,080	19-21	19,540
(1) To Kerosine, stove oil, tractor fuel					
(2) Gas oil: to cracking unit	1390 b/d				
to Diesel oil	1000 b/d				
(3) Existing units' bottoms:					
to cracking unit	9680 b/d				
to fuel oil	400 b/d				



A portion of the Pemex refinery pumping facilities is shown in this photo of the "A" manifold assembly and main transfer pump house

with the atmospheric tower is the extensive use of intermediate reflux. This was done for two reasons. The employment of intermediate reflux permitted a maximum recovery of heat and, therefore, a minimum consumption of fuel.

The use of intermediate reflux also saved considerable quantities of critical materials, since it made possible the use of a smaller tower and smaller furnaces. Savings in investment cost are always welcome when economically justified, but they were especially important at the time this plant was under design in view of the shortage of all materials because of the war effort.

It is to be noticed in Fig. 3 that the intermediate reflux points occur immediately below the drawoff points of the respective sidestreams. Each intermediate reflux stream was designed to remove the total reflux heat required in the section of the tower immediately below that stream. In order to obtain flexibility in the specifications of products made in this tower, several drawoff connections are provided for each sidestream. Several corresponding drawoff and return connections were provided for the intermediate reflux streams. Thus, regardless of the drawoff point of a particular sidestream, it is always possible to supply intermediate reflux immediately below that point.

One other minor point that may be worth mentioning is the use of a sand filter on the kerosine stream to storage whereby any traces of water carried out by the kerosine stream are coalesced and removed.

The depentanizer, which is also shown on the same flow sheet, represents the first step in the isobutane-isopentane recovery system. The feed to this unit is not only the total naphtha recovered in the new crude distillation unit, but also similar naphtha recovered from existing modified distillation units, which will be discussed subsequently, and hence represents the total C_4 375° F. end point material brought into the refinery with the crude.

Two design features perhaps should be briefly discussed. In view of the fact that the feed will undoubtedly contain some hydrogen sulfide and is therefore corrosive, complete elimination of water seemed to be desirable in order to minimize corrosion in this equipment, hence the use of a coalescing filter in the feed to this tower. By the use of the filter, it is expected that any moisture other than dissolved moisture picked up by the naphtha in intermediate storage will be removed before the naphtha is introduced into the tower, and severe corrosion due to the presence of hydrogen sulfide and water will be avoided.

Naphtha is substantially completely depentanized in this unit, primarily because a part of the depentanized naphtha is to be used to prepare base stock for aviation gasoline, and it is highly desirable to eliminate normal pentanes as much as possible from this material. Another advantage in substantially complete removal of pentanes and lighter from this naphtha was the reduction in storage losses for this material, which for the same vapor pressure product would be higher at the refinery elevation than at sea level.

A portion of the depentanizer bottoms is delivered to the base stock tower for the production of base stock for aviation

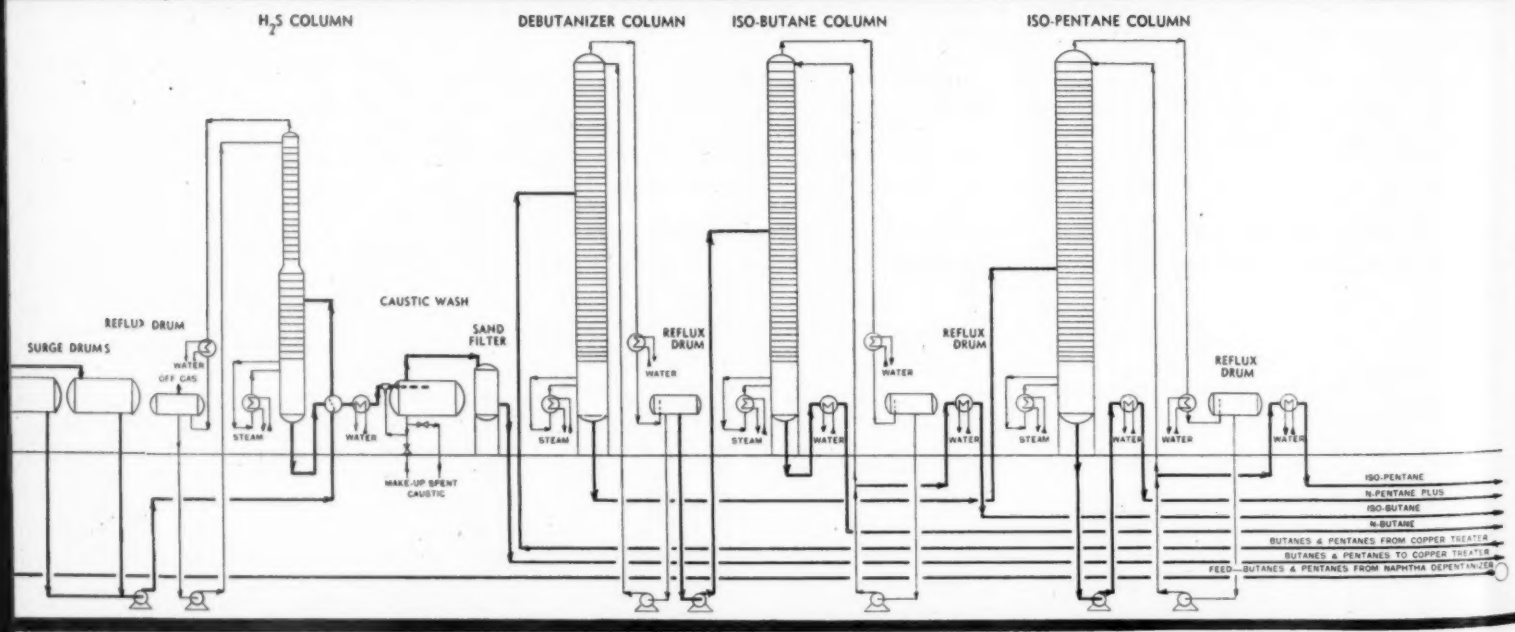


Fig. 4—Simplified flow diagram for the isobutane-isopentane unit

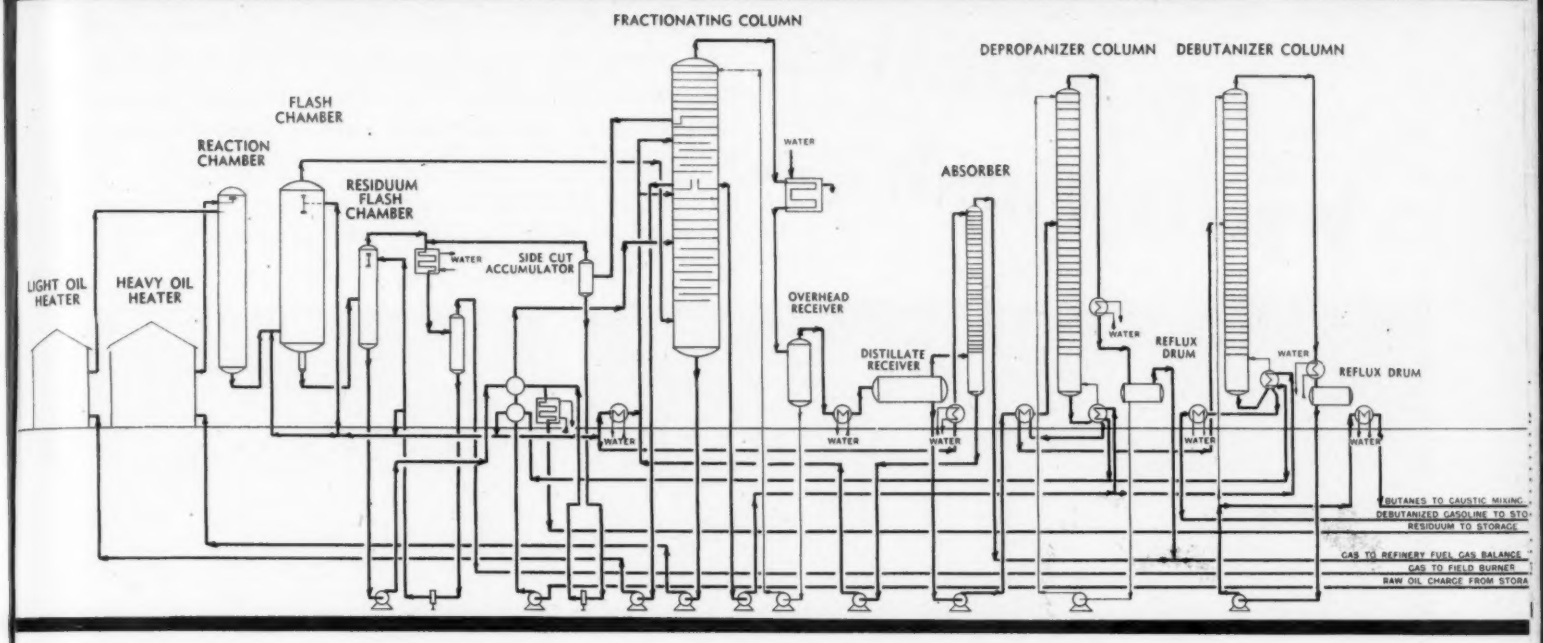


Fig. 5—Simplified flow diagram of the thermal cracking unit, licensed to Pemex by Universal Oil Products Co.

gasoline. The arrangement of the unit is such that the feed to the base stock tower may flow directly from the depentanizer to the base stock tower or may first be treated and then delivered to the base stock tower. Base stock is recovered as an overhead product from this tower. The bottoms from the base stock tower are combined wth the remainder of the depentanized naphtha and become a component of 60 octane number gasoline.

The production of a good aviation base stock presented a rather difficult problem. There is very little high quality base stock material in Poza Rica crude oil. To recover what little there is requires a considerable investment in fractionating equipment since a number of towers are required to separate a good quality base stock out of the heart of a straight run naphtha.

This did not seem to be justified either economically or from the standpoint of critical materials. After considerable study of the economic, technical and material aspects of the problem, it was decided that the preparation of a stream comprising constituents boiling in the range hexane to about 190° F. represented an acceptable compromise of all the factors.

Changes to Existing Crude Units

The existing crude units were originally designed for a simple topping operation of the crude oil. It was expected that these units would perform the same functions in the enlarged refinery picture and they could therefore have been left unchanged were it not for the fact that the projected crude supply to Atzcapotzalco would be enriched with natural gasoline, thereby making impossible complete condensation of the naphtha overhead cut prepared in an atmospheric distillation unit. It is true these existing units were equipped with preflash towers. However, they were not suitable for operation under pressure, and it was therefore necessary to replace these flash towers with a flash tower suitable for pressure operation.

In view of these considerations it was decided that the existing flash towers would be replaced by a single flash tower identical in design with the flash tower on the new crude distillation unit. In this way it will be possible at any time to replace the existing atmospheric towers by a single tower duplicating that used in the new crude unit. When this is done Pemex will have two identical modern distillation units, with the evident advantages in operation and maintenance.

On the basis of design of the expanded facilities, it is expected that the remodeled existing distillation units will produce (1) an overhead naphtha which will be combined with the overhead naphtha from the new distillation unit for further processing, (2) a kerosine sidestream which will be combined with the kerosine produced in the new distillation unit, and (3) a topped crude which will serve primarily as charging stock for the thermal cracking unit.

TABLE 3—Straight Run Fractionation

Feed and Products Design Conditions	B/CD	°API
Charge:		
Butanes and pentanes . .	2870	100-104
Products:		
Isobutane (Part of alkylation feed stock) . .	280	118
n-Butane (to LPG, motor gasoline, and isomerization unit)	1210	112
Isopentane (Aviation and motor gasoline)	350	95
Isopentane tower bottoms (motor gasoline)	990	89- 92
Fuel gas (Propane, hydrogen-sulfide)	30 MCF/D	

Straightrun Products Treating and Fractionating Units

The approximate feed to these units and yield of products are given in Table 3, while the flow is given in Fig. 4. The whole question of treating not only the straightrun products but also the cracked products was a subject of considerable intensive study and only the major factors which influenced the selection of the processes adopted for this plant will be outlined here. The general problem of treating comprised six parts:

(1) Hydrogen sulfide removal from light straightrun products.

(2) Treating of straightrun gasoline.

(3) Mercaptan removal from the butane-pentane stream.

(4) Treatment of butylene-amylene stream.

(5) Treatment of aviation base stock.

(6) Treatment of cracked gasolne.

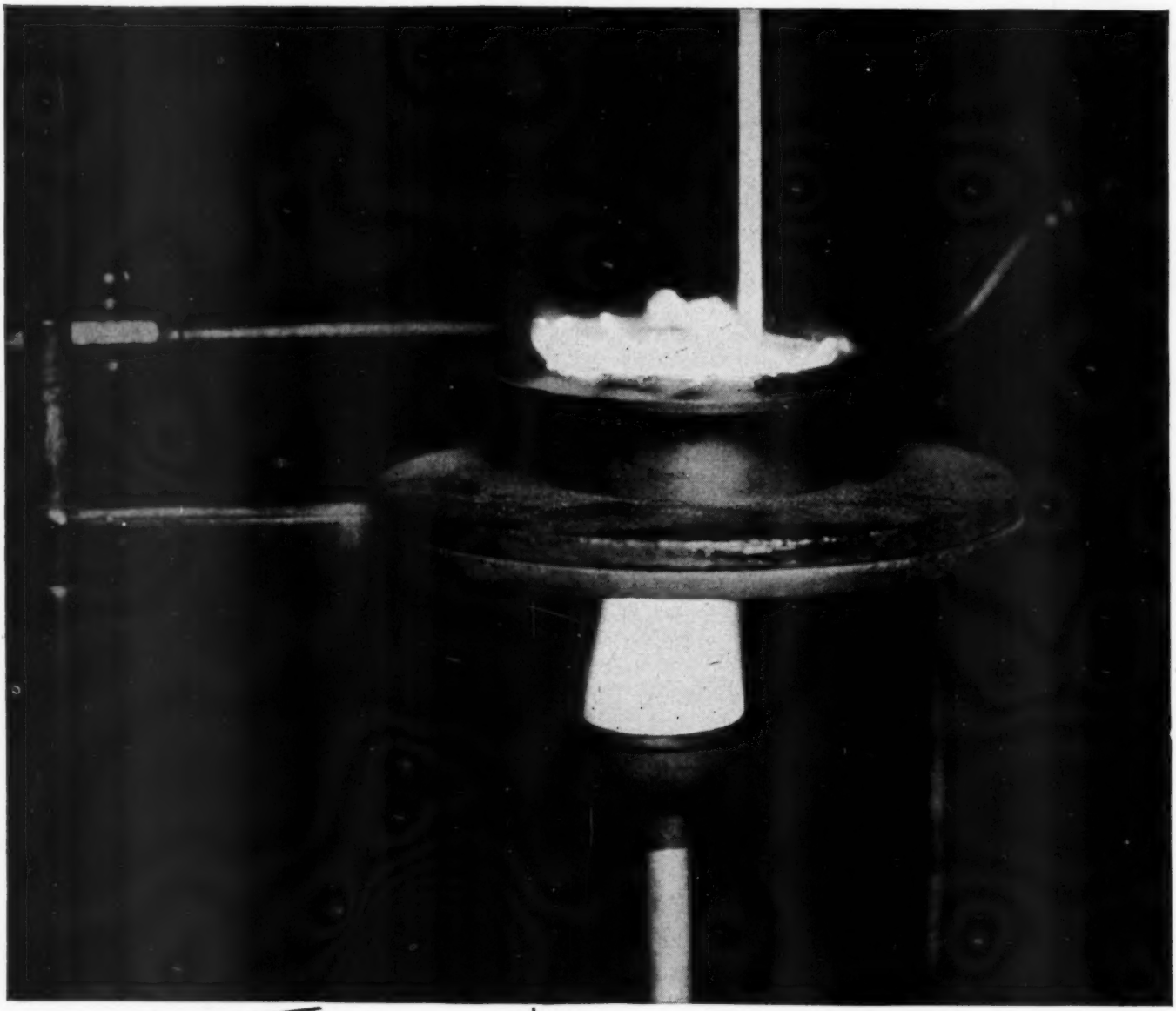
To the above list should be added, of course, the treatment of kerosine and Diesel fuel. These, however, presented

You Can't Select an Additive by its Flash . . .

but even routine tests are necessary in establishing the desirability of an additive for specific use.

Snapped at the instant of flash, this standard test is one of many conducted by Du Pont technicians to determine the effect of experimental additives on the physical properties of finished lubricants.

E. I. du Pont de Nemours & Co. (Inc.), Petroleum Chemicals Division, Wilmington 98, Del.



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no design problem in this case since it was evident that existing equipment would be adequate for the treatment of these stocks, at least for the immediate future.

In the treatment of the various stocks the removal of hydrogen sulfide is obviously the first step in all cases. Three general procedures are available. The simplest is probably a caustic soda or lime wash, however, this method was immediately ruled out because of the pollution problem which would be introduced. Local conditions, including proximity to Mexico City, render it essential that extreme care be taken to avoid pollution of effluent plant water as well as air contamination.

Two other methods are available for removal of hydrogen sulfide—stabilization and regenerative extraction. Of these two methods the choice was based entirely on economics and consumption of critical materials. Careful study and comparison indicated in this case that the removal of hydrogen sulfide from light straightrun products by stabilization was the preferred method. In this case stabilization served two purposes. It not only removed hydrogen sulfide from the butane-pentane stream but also removed final traces of propane brought to the refinery in the crude charge.

The question of hydrogen sulfide removal from straightrun products involved not only the choice of the process but the relative position which it should occupy in the plant flow. In the case of straightrun products the problem became the removal of hydrogen sulfide before or after the depentanizer.

If hydrogen sulfide were removed before the depentanizer, corrosion in the depentanizer would be reduced. On the other hand, the hydrogen sulfide tower would have to be considerably larger in view of the large quantity of straightrun naphtha which would have to be processed through the tower.

Thus hydrogen sulfide removal prior to depentanizing would require more construction material than after depentanizing. Because of this and because of the fact that corrosion in the depentanizer could be held to a minimum if the distillation were conducted in the substantial absence of water, it was decided to depentanize first.

Somewhat similar problems arose in connection with the treatment for mercaptans as in treatment for the removal of hydrogen sulfide. Several processes are available. These may generally be divided into: extractive, such as regenerative caustic, Unisol, or tannin solutizer; destructive, such as Perco catalytic clay; and conversion, such as "doctor" treat or Perco's copper chloride. Ideally, one of the first two enumerated methods should be preferred since these eliminate sulfur from the system.

The Unisol and tannin solutizer processes were considered carefully and both had important advantages but requirements for chemicals not available in Mexico and requirements for critical construction materials finally led to the rejection of both processes for this project.

The regenerative caustic soda process is a satisfactory way of removing mercaptans, especially the lighter mercaptans, from hydrocarbons. The efficiency of this process decreases appreciably as the molecular weight of the mercaptans increases and comes about in two ways, namely, a lowered extractive efficiency, and also a lowered regenerativ efficiency.

For the present case this process had the advantage over the other extractive processes in that it was more economical in equipment and simpler to operate than the other two extractive processes. Furthermore, equipment installed for regenerative caustic treating could very readily be converted to tannin solutizer treating by addition of other equipment at a later date. The one disadvantage in regenerative caustic treating of gasoline was that the final product, while satisfactory from the standpoint of use, might not under certain conditions pass the "doctor" test.

The destructive process for mercaptan removal had a number of attractive features. However, the initial cost and consequent construction materials requirements were estimated to be somewhat higher than for the extractive processes. In view of these factors, catalytic clay treating was not used.

The conversion treating processes involving the conversion of mercaptans to other sulfur compounds have been used successfully for years. The main disadvantage compared to the processes referred to earlier, is that no sulfur is eliminated from the product, in fact in the case of doctor treating some sulfur may be added to the final product. Insofar as the treating of lighter straightrun products to be used for manufacturing aviation gasoline is concerned, this method of treating would be satisfactory due to the fact that the disulfides and heavier sulfide compounds formed could be separated from those products by subsequent distillation, thereby giving sulfur-free material for the preparation of alkylate.

However, the disadvantage in this process was that it threw all of the sulfur into the 60 octane number gasoline, thereby possibly increasing the TEL requirements. A comparison of doctor sweetening versus Perco copper chloride treating indicated that the latter was a simpler process to operate and would require less critical materials.

On the basis of all the factors outlined above, and other minor ones not mentioned, it was decided that the treating for mercaptans of the straight run products, i. e., butane-pentane stream, the aviation gasoline base stock, and the straight run motor fuel, would comprise the Perco solid copper chloride process, as developed by the Phillips Petroleum Co.

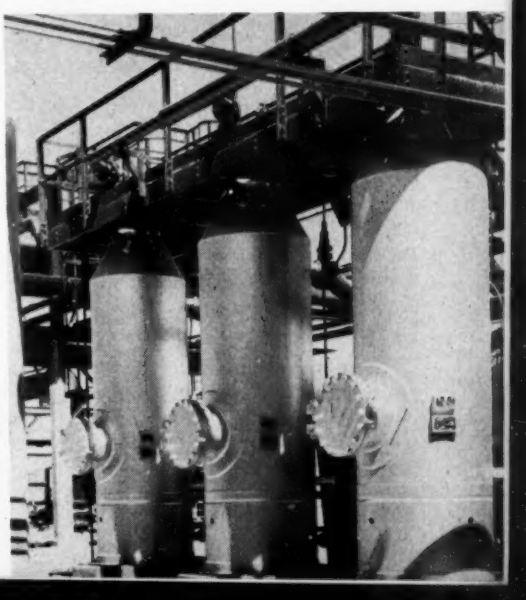
One question still remained, namely treatment of the butane-pentane stream as a single stream or fractionation first into the components finally required and then treatment of each component separately.

The main disadvantage in treating the total butane-pentane stream before fractionation is that the normal pentanes in the stream which are subsequently eliminated in the isopentane tower are treated, thereby requiring somewhat larger treating equipment. However, comparison of the two ways of treating indicated that treating the combined stream not only would be more economical of equipment, but also would eliminate sulfur compounds from the isomerization unit, alkylation unit, and aviation gasoline, since these compounds would all concentrate in the isopentane tower bottoms. The plant was therefore set up on this basis.

The butane-pentane stream from the bottom of the hydrogen-sulfide tower is first passed through the treating plant and then fractionated into isobutane, normal butane, isopentane, and isopentane tower bottoms which comprise the residual isopentane, normal pentane, and heavier, and also substantially all of the disulfides and heavier produced in the treating unit. These bottoms are blended into the 60 octane motor fuel.

The base stock preparation is arranged to operate in either of two ways. In one, the preferred way, a portion of the depentanizer bottoms is first passed through the Perco base stock tower feed treater, and then sent to the base stock tower. In this way there will be sub-

Sand filters at the cracking unit for the caustic treater B-B cut



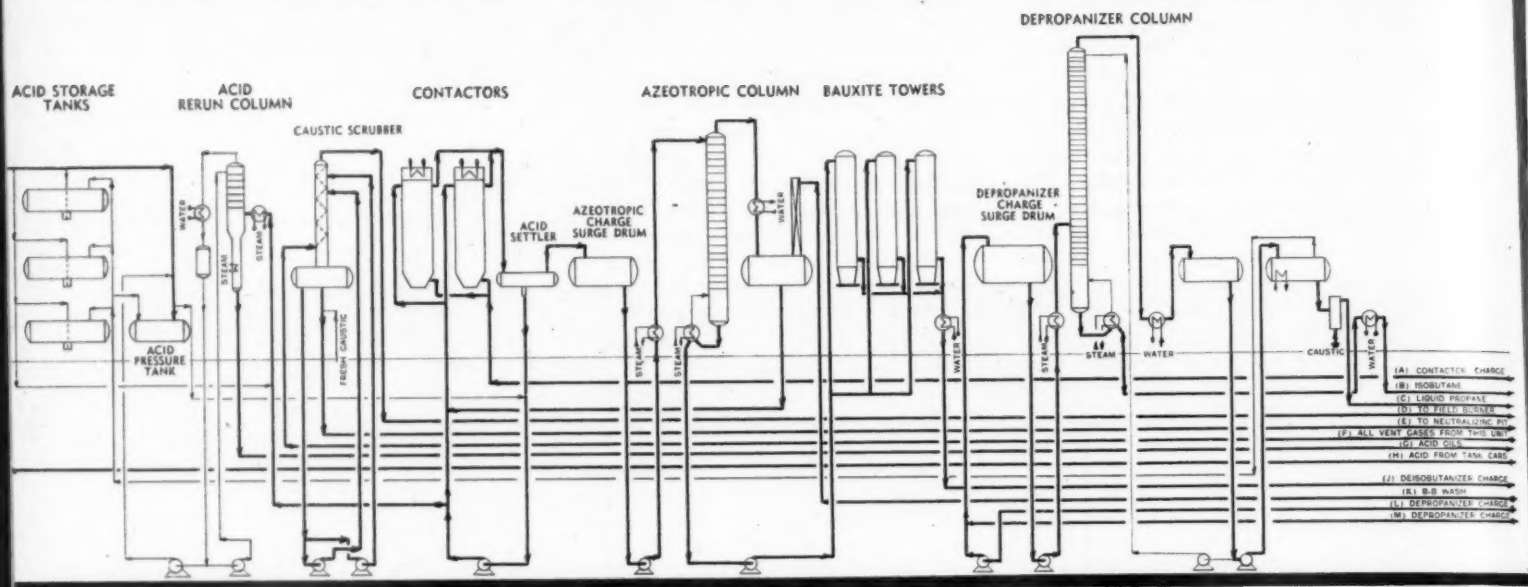


Fig. 6—Shown across both pages is a simplified flow diagram for the HF alkylation unit

stantially no sulfur in the base stock since the higher boiling disulfides, etc., are formed prior to distillation and are removed from base stock in the base stock tower since these sulfides will leave the column along with the heavier bottoms. The overhead base stock product can be sent directly to storage or it can receive another treat in the Perco base stock treating unit.

In the alternate way of operation, hot dependanizer bottoms may be charged directly into the base stock tower; the base stock removed as an overhead product and sent to the Perco base stock treater before going to storage. The advantage in this operation is a slight saving in heat but the disadvantage is that the sulfur originally present in the base stock would still be there after treating and would eventually show up in aviation gasoline. However, this would not be expected to be a severe disadvantage in view of the fact that base stock forms such a small portion of the aviation gasoline.

Thermal Cracking Unit

Approximate feed and products for the thermal cracking unit are shown in Table 4, while the flow through the unit is shown in Fig. 5. This unit was licensed and designed by the Universal Oil Products Co. It is a two coil selective cracking unit and includes a depropanizer and debutanizer for the preparation of a butylene-amylene feed stock for the alkylation unit.

There are a number of features of interest. Perhaps foremost is the employment of UOP's equiflux type furnaces for both the light and heavy oil coils, thereby assuring optimum conditions for heating and cracking of the respective stocks. These heaters, in addition, are equipped with waste heat boilers, for it is not only economical but essential that heat recovery be carried to as great an extent as possible. In this case some 40,000 lbs./hr. of 50 psi steam are generated in the waste heat boilers.

Corrosion protection, while not as extensive as it might be had this unit been designed under normal conditions, was carried as far as possible consistent with the supply of critical materials. The necessity for more than average corrosion protection is apparent when it is recalled that Poza Rica crude is a relatively high sulfur crude with most of the sulfur appearing in the residual stocks, and hence in the feed to the cracking unit. In order to reduce corrosion in the heater tubes and in parts of the fractionating system, lime injection into the heavy oil coil is practiced. This feature, together with judicious use of suitable alloys, is expected to give long life to the unit.

The depropanizer and debutanizer have been designed with a considerable amount of flexibility to allow for the production of an alkylation unit feed stock of wide characteristics as may be required by the demands of the refinery.

There is considerable latitude in the amount of propylene or amylene in the debutanizer overhead.

Finally, looking ahead to the day when waxes and lubricating oils are manufactured at Atzcapotzalco, at which time the charge to the cracking unit will be gas oil rather than topped crude, UOP incorporated into the design such features as were necessary to permit the cracking of gas oil rather than topped crude.

In view of the fact that hydrogen sulfide has been removed from the butylene-amylene stream in the depropanizer tower in the cracking unit, hydrogen sulfide removal facilities are not required in the treating unit proper. The treating unit adopted for reasons outlined in the section "Straightrun Products

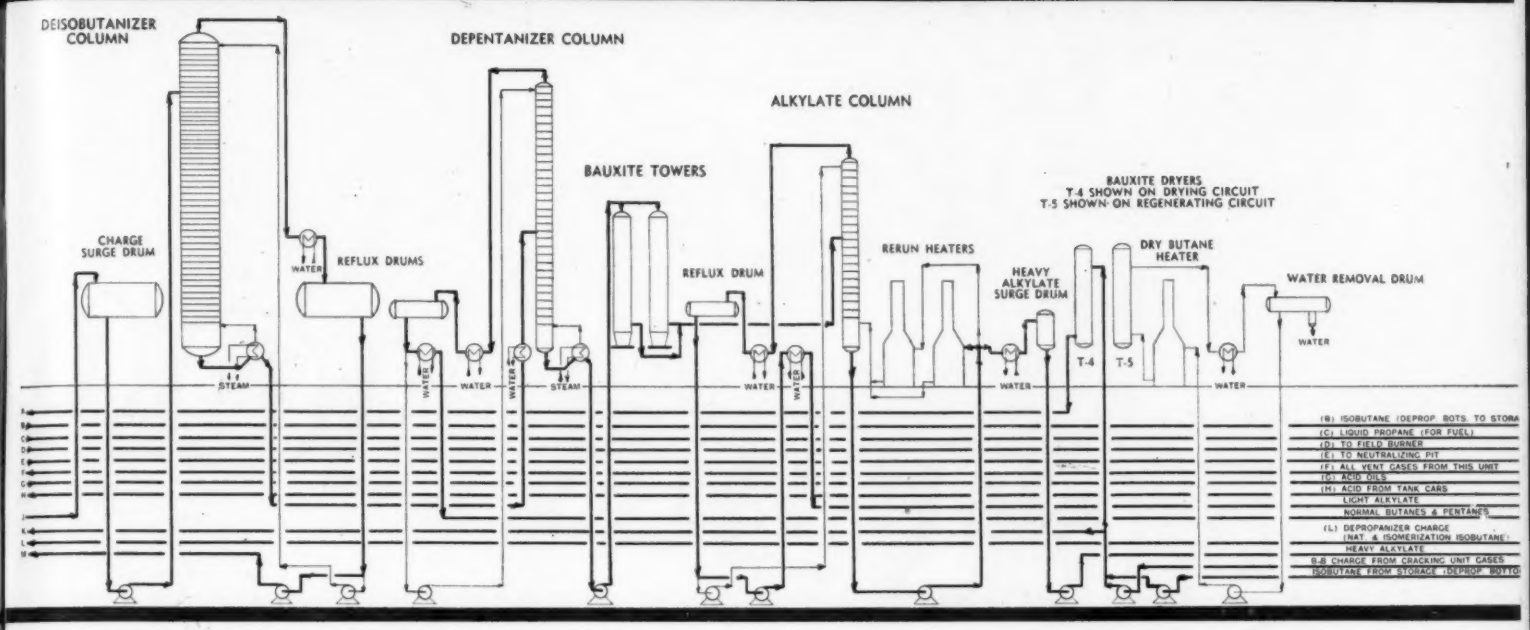
TABLE 4—UOP Thermal Cracking Unit

Feed and Products Design Conditions	B/CD	°API
Charge:		
Poza Rica topped crude	9680	19- 21
Gas oil	1390	33- 35
Total blend	11,070	19- 21
Products:		
Alkylation unit olefin feed stock	870	105-108
Motor gasoline stock	4000	56- 58
Fuel oil	5830	7- 9
Fuel gas	3610 MCF/D	

TABLE 5—Isomerization Unit

Approximate Charge and Products(1)	B/CD	°API
Charge:		
Normal butanes	350	112
Products:		
Isobutanes	250	118
Normal butanes	100	112

(1) Figures represent expected requirements from the isomerization unit. Actual design of unit considerably in excess of these quantities.



at the Atzcapotzalco refinery, licensed to Petroleos Mexicanos by Phillips Petroleum Co.

Treating and Fractionating Unit" is a three-stage regenerative caustic unit. The only unusual feature worth noting perhaps is the employment of sand filters to coagulate final traces of moisture that may be carried in suspension by the effluent hydrocarbon stream, thereby possibly reducing the load on the bauxite driers in the alkylation unit, and also avoiding any caustic carry-over into the alkylation unit.

Butane Isomerization Unit

The approximate feed and products are shown in Table 5. Shell Development Co. licensed the liquid phase butane isomerization unit to Petroleos Mexicanos and supplied the requisite process and mechanical design data.

The inclusion of a butane isomerization unit into the expanded Atzcapotzalco refinery received considerable study before its adoption. The use of such a unit had two important advantages: a considerable increase in flexibility in the refinery and in the fields, and a decrease of emphasis on isobutane availability and recovery at Poza Rica.

One of the large question marks in the design of the whole project was whether there would be, at the time of plant operation, as much isobutane available from the field gases at Poza Rica as early tests and analyses indicated. From these, it was evident that a high recovery of the isobutane indicated to be present in the crude oil natural gas would be required to satisfy the requirements of the alkylation unit at the projected capacity; thus, the success of this particular aviation gasoline project was highly dependent on the factor of isobutane availability, over which there was limited control.

Employment of a relatively small butane isomerization unit assured adequate supply of isobutane independent of the production at the Poza Rica field. Once a decision was reached to employ such a unit it became evident that it was no longer necessary to strive for high butane recovery at Poza Rica, and thereby substantial savings were effected in critical materials.

Opposed to these important advantages in the use of a butane isomerization unit were the disadvantages that the refinery now included a new refinery unit which required a somewhat different operating technique and employed a new catalyst, thereby complicating in some measure the overall refinery picture.

The choice of the liquid phase butane-isomerization process as developed and licensed by Shell was made after considerable study of all the processes then available. The possible future use of this process for hydrocarbons higher than butane represented one factor of importance in arriving at the decision to use this isomerization method.

It should be noted that an isobutane column is supplied in connection with this unit. While the separation of isobutane produced in this unit from residual and normal butane could have been effected in one of the other isobutane towers in the refinery, such as in the straight run fractionating unit or the alkylation unit, it was decided to keep this fractionation separate in order to give the refinery the best chance for long continuous runs by not tying up several processing units with a common isobutane tower which could become fouled up by chemical carry-over, or otherwise be made inoperative. In this way if there be an upset in one unit—for example, the isomerization unit—it would not affect all the other units in the refinery, and thus there will be less interference with production of aviation gasoline and other products.

HF Alkylation Unit

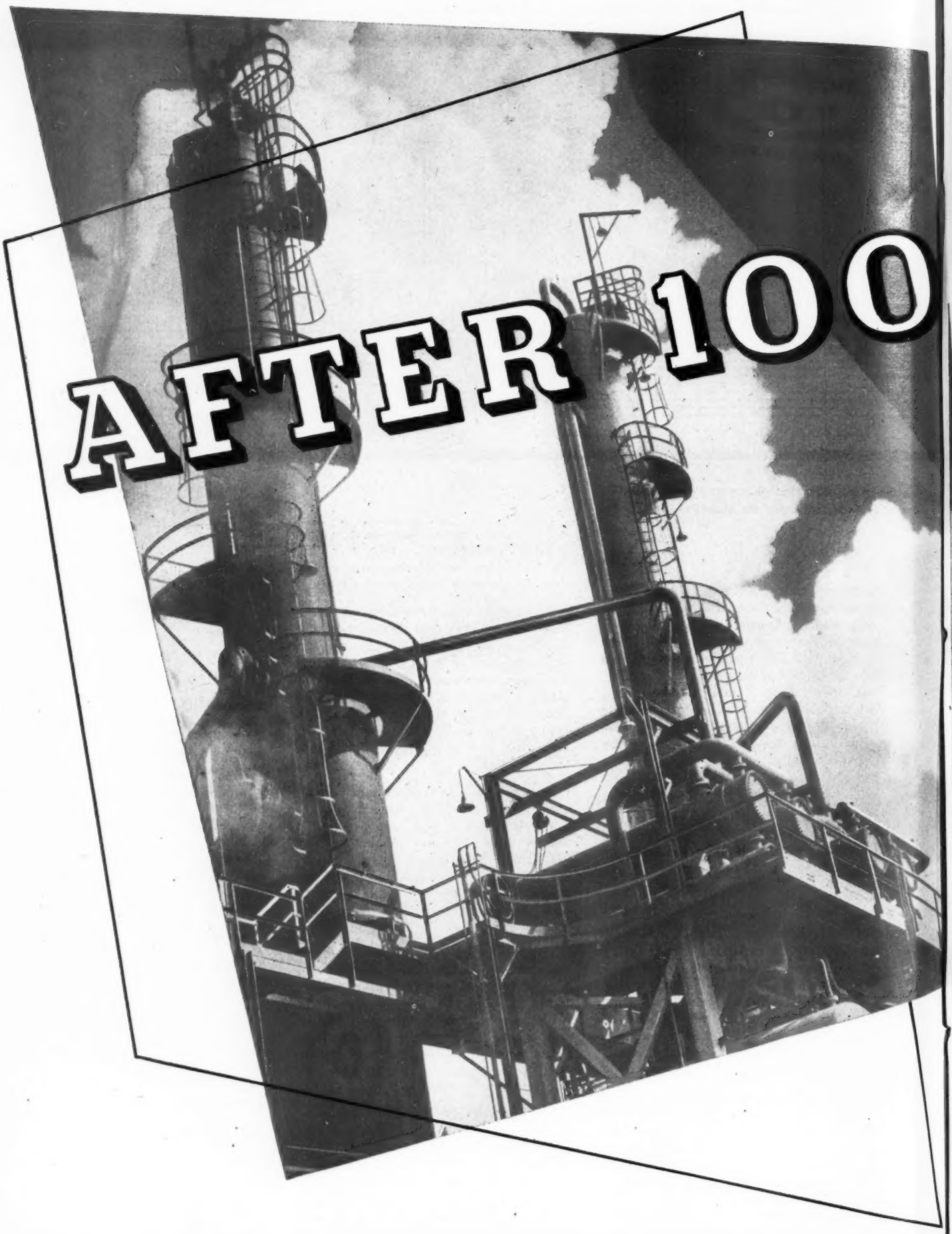
The approximate feed and yield of products for the alkylation unit are given in Table 6, while flow through the unit is outlined in Fig. 6. Phillips Petroleum Co. licensed this unit to Petroleos Mexicanos and supplied the requisite process design and engneering data.

This alkylation unit was designed late in the war construction period and therefore had the advantage and opportunity to incorporate in its design all improvements resulting from operating experi-

TABLE 6—H. F. Alkylation Unit

Feed and Products Design Conditions

	B/CD	°API
Charge:		
Isobutanes	545	118
Olefins (from cracking unit)	870	105-108
Total blended feed	1415	110-113
Products:		
Light alkylate (to aviation gasoline)	690	62- 64
Heavy alkylate (to motor gasoline)	15	40- 43
Butanes-pentanes (to motor gasoline)	460	104-107
Water and tars (loss)	6	.....
Fuel gas (propane)	105 MCF/D	


AFTER 100

OCTANE, What?

Between 1941 and 1945 the American Petroleum Industry performed one of the greatest industrial miracles of all time. As the world knows, it was the quantity production of 100-octane gasoline. Production rocketed from a bare 40,000 barrels daily in 1941 to over 500,000 barrels daily. Even the rating 100-octane was left behind.

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ence on the earlier units. This condition applied not only to the process design of the unit, but also and possibly more especially to the mechanical design and the selection of materials for especially corrosive services. As is to be expected, these improvements are primarily in detail items rather than major items. It is therefore not feasible at this time to attempt a complete summary of these improvements, but the following examples are given by way of illustration.

Accumulation of water was one of the problems in earlier plants. To eliminate this water, a water removal tower had to be incorporated in the acid rerun system. Because of the severe service, suitable materials of construction sufficiently resistant to the severe corrosive conditions were difficult to find. In this alkylation unit the total stream to the contactors is first fed to the depropanizer column. Here a considerable portion of water brought into the system by the various feed streams is removed as an overhead product together with propane. Supplementing this the total hydrocarbon stream to the contactors is passed through the bauxite driers prior to its introduction into the acid section of the plant.

By this combination no water whatever is allowed to enter the acid system and therefore no facilities for removal of water from the acid system need be provided. The use of the depropanizer as outlined above reduces the load on the bauxite driers, thereby making possible longer runs between periods of revivification.

The gases (propane and lighter) leaving the system from the azeotropic fractionating tower overhead accumulator are passed through a small packed tower which is refluxed with a portion of the olefin feed to the plant. These olefins react with any hydrogen fluoride that may be present in the light gases, forming organic fluorides, thereby returning to the system any hydrogen fluoride which would otherwise have been lost; thus hydrogen fluoride losses are reduced. This is probably a more important factor in Mexico than it would be in the United States, since all hydrogen fluoride must be imported.

There is no provision in the alkylation unit fractionating system for separating normal and isopentane, since sufficient isopentane is available to satisfy all the blending requirements of the refinery. Incidentally, the alkylate depentanizer is designed for substantially complete removal of normal pentane from alkylate with substantially no alkylate in the pentane stream. By this method of design and operation it will be possible to use greater amounts of isopentane in the aviation gasoline blend, thereby obtaining more or better aviation fuel than would be possible had some normal pentane been left in the alkylate.

Boilers and Power Generation

The refinery at Atzcapotzalco is primarily motor driven and the new facilities include equipment to produce all required electricity. Total electrical requirements, including lighting usage, are provided by two 5000 KW steam turbine driven generators, one acting as standby. Three fuel oil and fuel gas burning boilers, each rated at 125,000 lbs. of steam per hour, supply the plant needs for power, processing and heating.

The turbines are of the mixed pressure type with inlet steam from the boilers at 600 psig and 750° F. and steam withdrawal at 275 psig and at 50 psig. Considerable steam is produced in the plant by waste heat boilers at about 50 psig and consequently provisions are made either to withdraw or to introduce steam at this pressure level in the power turbines. The balance of the steam not utilized in the plant at the 275 lb. or the 50 lb. level passes through the turbines and is condensed in the usual manner.

To a considerable extent steam is used for process heating and reboiling and provisions have been made to return as much condensate as possible from all sources to the boilers in order to minimize the requirement for raw makeup feed water.

Water Supply System

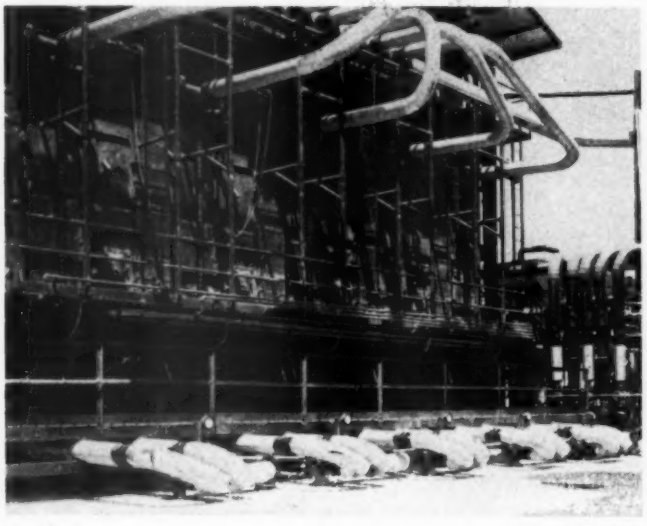
Four deep well pumps supply the required make-up water to the forced draft cooling tower and the boiler plant at approximately 2000 gpm. Water supply to the more corrosive sections of the processing units is kept segregated from the balance of the equipment. The cooling tower is divided into two sections: one supplying coolant for the alkylation and the isomerization units at about 6000 gpm; the other supplying the necessary water to the remainder of the refinery units, the boiler plant, and the fire hydrants.

Two pumps furnish water at about 5000 gpm to the boiler plant. Three pumps deliver water at about 26,000 gpm to the thermal cracking unit, the three crude distillation units, and the isobutane-isopentane unit. The fire hydrant system is equipped with a 2000 gpm pump.

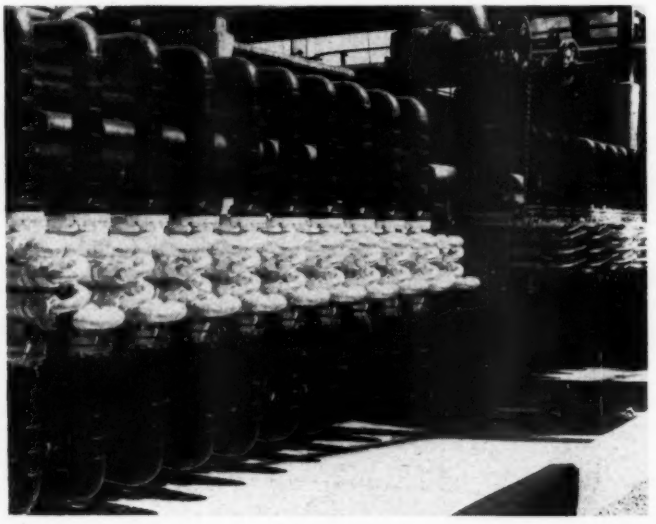
Storage Facilities

Although only minor additional storage facilities were needed for incoming crude oil, considerable tankage has been added for process and finished product storage. The existing tanks, mostly atmospheric storage, total about 870,000 bbls. They have been augmented by an additional 61 vessels, providing about 600,000 bbls. atmospheric storage, and 75,000 bbls. pressure storage for isopentanes isobutanes, butanes and other light stocks.

Process heat for the thermal cracking unit is supplied by this Universal Oil Products Co. equiflux furnace



Thermal cracking unit heat transfer between residue and charge stock is provided by this bank of heat exchangers



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PLANT PRACTICES

Practical Tips and Ideas for Improving Refinery Operations

Uniform Gaskets Can Be Cut Quickly and Accurately from Vinylite Plastic Tubing

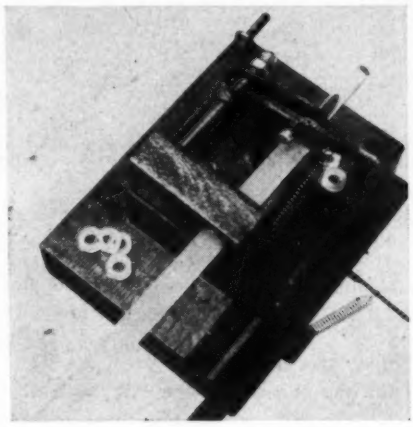
By A. B. KOURT, Phillips Petroleum Co.

VINYLITE plastic gaskets are used on laboratory vapor-pressure bombs to protect the ground seat joints between the gasoline and air chambers. They have been difficult to obtain and the expedient of making them from men's plastic belts by cutting them out with a knife was adopted.

Then a suggestion that they be cut from ⅜-in. O. D. by ⅛-in. wall vinylite plastic tubing was made. The particular value of the tubing is that it was already of the desired inside and outside diameters and, for use as gasket material, needed only to be cut to the desired thickness. In addition, the tubing was a much more economical source of supply than the plastic belts.

A suggestion was for the use of a specially-designed gasket cutter. This cutter is shown in the photograph and also in the detail drawing, Fig. 1. It not only saves time but also provides gaskets of uniform thickness since it can be set accurately. Cutting the tubing with a knife often resulted in gaskets of uneven thickness.

The cutter consists of a wood base, two wood blocks, a metal plate, a bolt knife-holder, razor blade, springs, and a glass rod. Mounted on the larger block screwed to the wood base, the plate carries a full-threaded 4-in. bolt. One end of the bolt fits into a socket in the second wood block, and a crank handle is attached to the head end.



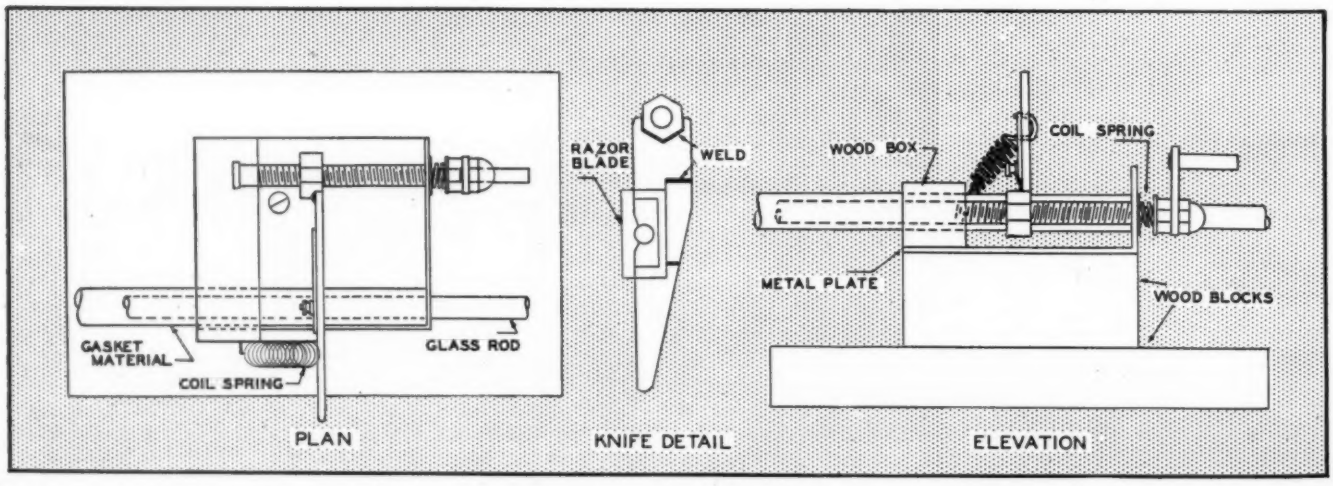
Above, photograph of cutter and some of the gaskets it makes. Below: Fig. 1—shows plan and elevation view and knife detail

A piece of sheet steel, welded to a second nut, is also carried on the bolt and is equipped with a thumb-screw and plate to firmly secure the razor blade, thereby acting as a knife-holder. A spring attached to the handle of this knife-holder provides pressure when the gasket is being cut. By means of the crank handle on the bolt, the cutter is adjustable to the various desired gasket thicknesses.

The glass rod supports the tubing during cutting and is supported at one end by the steel plate and at the other by the wood block. The hole in the wood block is large enough to take the tubing, while that in the plate will take only the glass rod.

In cutting operations the vinylite tubing is placed in the tool; the knife edge is adjusted so as to cut the proper thickness and is allowed to rest firmly against the tubing, being held down by the coil spring. The operator then rotates the tubing until the razor edge has cut through to the glass rod. Then he lifts the knife and moves it forward the desired distance by means of the crank, and repeats the cutting operation.

Before using the vinylite gaskets, the laboratory was replacing one round seat joint daily, on the average, because of leaks from scoring. Poorly cut gaskets also were a contributing factor, and replacements from this cause have been entirely eliminated.



Liquid Level Recorder Design Minimizes Difficulties in Alkylation Unit Settler

By ALFRED KRIEG, Supervisor, Instrument Department
Socony-Vacuum Oil Co., Inc., Paulsboro (N. J.) Refinery

LIQUID level measurement and control on hydrofluoric acid alkylation units is a difficult job, primarily because of the accumulation of fluorides on moving parts. These salts bridge the small clearances and cause increased resistance and eventual binding.

The Instrument Department at Socony-Vacuum Oil Co.'s Paulsboro (N. J.) refinery overcame this instrumentation problem on a recent installation by using floats and electro-magnetic transmitters.

In HF alkylation, the hydrocarbon charge stocks and the acid are combined in a contactor where complete mixing and treating takes place. This mixture then flows to a settler where the hydrocarbons and acid separate and are pumped to their respective processing units.

An indication of the hydrocarbon level and a control of the interface or acid level is very critical to process operation and it is important that the instruments perform continuously and accurately. Similar units throughout the country have experienced considerable trouble with these installations. One of the chief difficulties as previously pointed out, was the accumulation of the fluorides on moving parts. Because of this induced friction and because of the acid service, the use of packing glands is prohibitive. With these restrictions in mind, the Instrument Department developed the method as shown in Fig. 2, consisting of two floats and electro-magnetic transmitters.

In order to assure continuous positioning of the armature within the inductance coil of the transmitter, the moving parts of the internal mechanism are made with loose clearances—thus minimizing the binding effect of the fluorides.

Since there is less than .3 difference between the specific gravity of the hydrocarbon and the hydrofluoric acid at operating temperature, the buoyancy effect on the ball float is relatively low, therefore the ball float must be of proper size and weight and the float arm of such length as to assure powerful leverage to position the armature.

With a change in the level of the hydrofluoric acid interface or the level of the hydrocarbon, the armature is positioned in the inductance coil of the transmitter. This is transmitted electrically to a controller or recorder in the control room. The transmitter is a standard electrically operated inductance type with minor modifications to suit the application.

Purging lines are connected into the armature tubes to permit continuous flushing with clear hydrocarbons to retard the accumulation of fluorides on the armature or the tube wall. This clearance is small and a slight accumulation would restrict the normal motion.

Because the hydrofluoric acid will attack pinhole inclusions which may be present due to welding, the monel ball floats were silver plated as a preventive measure.

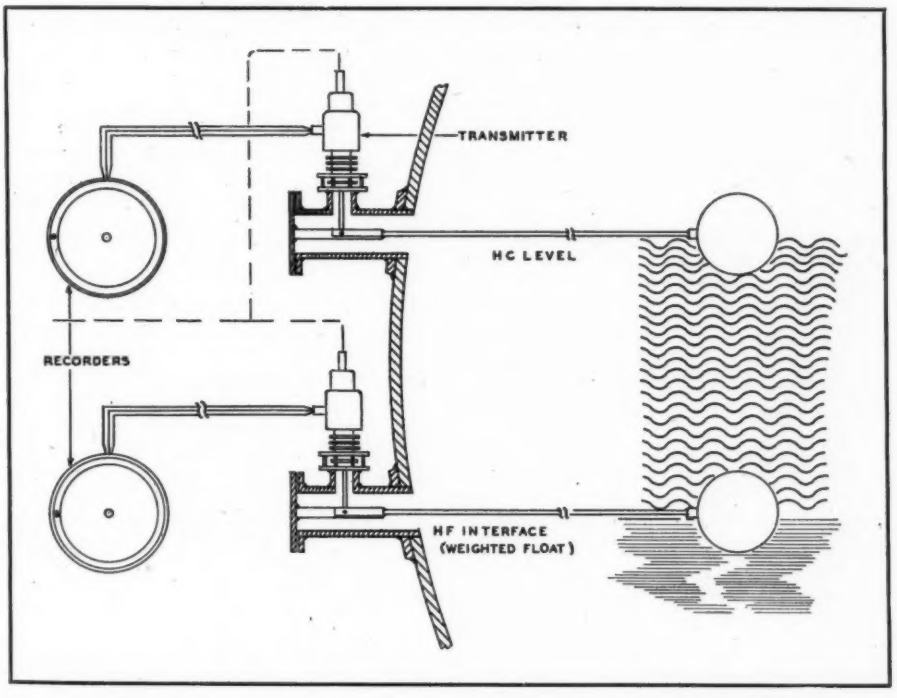


Fig. 2—Liquid level recorder for HF alkylation unit acid settler. Purging lines connecting into the armature tubes permit continuous flushing with clear hydrocarbons to retard accumulation of fluorides

Filter Eliminates Plugged Lines In Pilot Plant Cat Cracker

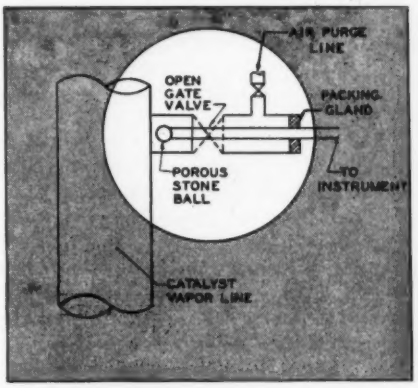


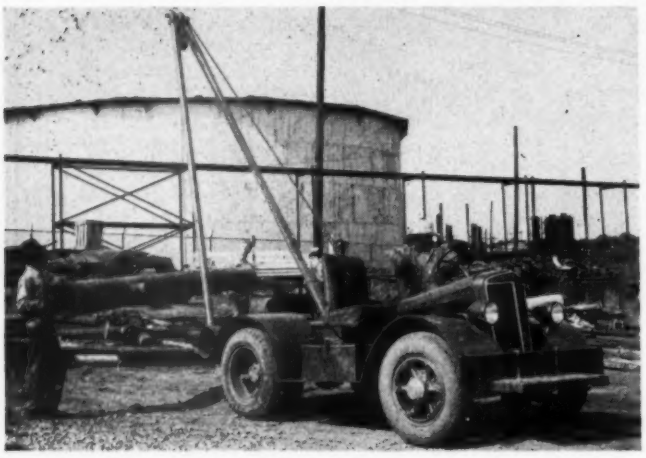
Fig. 3—Porous stone ball filters on instrument lines prevent plugging

IN the operation of small pilot plant Fluid Catalytic cracking units, high purge rates on instrument lines are not permissible if conditions comparable to the full scale unit are to be maintained. Since the whole system is small, pressure surges are frequent and lines are quickly plugged with the catalyst. Such circumstances often require bringing the unit to shutdown in order to unplug the lines.

An ingenious instrument repairman at the Baytown plant of Humble Oil & Refining Co., J. L. Matthews, was awarded a prize in the company's job-suggestions program by proposing that porous filters be placed over the end of the instrument line to prevent catalyst entry. His solution to the difficulty is shown in Fig. 3.

The original instrument lines were removed and a connection installed which is large enough to take the instrument line equipped with a porous stone filter ball. This line is equipped with a packing gland through which the line from the instrument passes, and also a gate valve, which must be open when the instrument line is in place. The usual air-purge line also is connected to the larger line, and used to permit periodic cleaning of the filter in addition to simulating operation of the commercial full-scale unit.

Shop-Built Material-Handling Buggies Are Versatile Helpers



Rugged construction of Continental Oil Co.'s fleet of shop-built material-handling units is shown in these photographs. Sturdy bumpers, winches, and gin-poles increase utility of the little units

CONTINENTAL OIL CO. has gone in extensively for the use of motorized equipment for refinery maintenance as well as in field work. It now has a fleet of small trucks—largely Fords and Chevrolets, ranging in sizes from ½ to ¾-ton pickups—which are equipped with power take offs, winches and gin-poles for hoisting heavy equipment in the refinery.

The gin-poles will lift from 750 to 1000 lbs., depending on size of truck and angle of the pole during the lifting. They are used to lift and hold pipe in place for fabrication, exchangers and other heavy or bulky items. Having short wheelbases (many were shortened in the refinery shops for the purpose) and superstructures as near the ground as possible, these power trucks can get into most places ordinarily considered inaccessable to this type of equipment.

In addition, by means of trailers, all the small tools and other items needed for a particular maintenance job can be hauled to the site at one time, saving many trips back and forth from warehouse or shops to the job.

Most of these trucks use 7.50-16 tires, 8-ply if possible, to withstand any load which gin-pole and engine are capable of lifting. Hoods have been reduced in size and radiators revamped and remounted to reduce overall vehicle height as much as possible. Two typical types are shown in the accompanying photographs.

IDEAS—Wanted!

Plant operators, foremen, superintendents — Send in your own original contributions on "how we do it around our refinery." Possible subjects could include operating shortcuts, time and money-saving gadgets, repair ideas, inspection procedures, accident and fire prevention schemes — anything which has made your refinery more efficient, safer, and easier to run. Include photographs, drawings, or sketches, if available.

Send your contributions to:

Plant Practices Editor
PETROLEUM PROCESSING
1213 West Third Street
Cleveland 13, Ohio

Drain Petcocks on Explosion-Proof Motors Are Not Good Practice, Readers Report

THE practice of installing drain petcocks on the casings of explosion-proof motors on intermittent service in a damp climate so as to reduce coil failures because of moisture accumulations is unsafe, it is reported.

An item in the Plant Practices section of the January, 1947, issue of PETROLEUM PROCESSING (pg. 17) described this operating idea. In practice, it was stated, operators are instructed to drain the water from the motor casing each time before starting the motor.

Two recent letters condemn this practice as hazardous. Mr. W. C. Westerberg, assistant chemical engineer, Underwriters' Laboratories, Inc., Chicago, Ill., said:

"We have tested and listed many explosion-proof motors for use in hazardous locations, Class I, Group D, but have not permitted the manufacturer of a labeled motor to provide drain petcocks, as it was the consensus that such fittings might be left open and thereby defeat the purpose of the explosion-proof construction.

"Our Standard for Explosion-Proof Motors specifies that drain plugs, if used, shall be permanently fixed automatic drains, and shall be accepted on the basis of adequate tests in each individual case. Labeled motors may, therefore, be provided with such automatic drains, which will permit the escape of condensed water . . ."

The electrical engineer for one midwestern refinery wrote a similar comment. He pointed out that because it is possible to leave such drain petcocks open unintentionally, the motor no longer can be classified as explosion-proof, and that, therefore, neither the motor manufacturer nor the Underwriters' Laboratories could assume any future responsibility for the motor being safe in Class I, Group D locations.

Do You Disagree?

Has your own experience proved to be different from those ideas, tips, and gadgets presented in this Plant Practices section? Have you developed a better method for solving the same operating or maintenance problem? If so, tell us about it. Send your comments, criticisms, and opinions to the Plant Practices Editor, PETROLEUM PROCESSING, 1213 West Third Street, Cleveland 13, Ohio.

UTOPIA—100% SAFE

Strict Tests Precede Each Utopian Tank Cleaning Job

Tests of vapor content in tanks—checks on air masks and other personal protective equipment—use of non-sparking tools—complete adherence to all precautionary measures—insure a perfectly safe operation for tank cleaning crews in the mythical refinery of Utopia.

By FRANK J. SLUZE, Safety Director
Ashland Oil & Refining Co.

OUR first stop on this month's inspection of the Tank Cleaning Department will be at the storage house. Inside we find non-spark tools such as scrapers, putty knives, scoop shovels, buckets, and bars. Looking around further we find respiratory equipment such as fresh air masks, gas masks, respirators, and air movers. We also see several trunks containing fresh air blowers, both hand and motor operated. An adequate supply of rubber boots, rubber gloves, rubber clothing, face pieces, breathing hose, and gaskets is also kept in this house, as well as a supply of gas tight goggles.

After leaving this point we see a tank that previously contained gasoline being made safe to enter for cleaning out the sediment. Upon closer observation we learn that it is being made gas free by steaming. It has been steamed a number of hours to raise the temperature in the tank to about 170° F. We notice that the top manholes have been left closed and that the steam is being introduced through a bottom manhole. The pressure and vacuum vents are open to prevent collapse of the tank because of quick change in temperature. To guard against the hazard of static electricity, the steam is adjusted to enter the tank at a low velocity and the steam line is bonded to the tank.

Induced Natural Ventilation

Having satisfied himself that the highest practical temperature has been realized, the tank cleaning foreman instructs the workers to shut off the steam and remove the top and bottom manhole covers so as to induce an internal circulation which will promote ventilation.

The foreman then calls for a petroleum vapor test, and the safety engineer arrives with his petroleum vapor indicator to perform the test. Because the vapor content is less than 14% of the lower explosive limit, the foreman concludes that no ignition can take place. However, since the tank is not completely gas free, the cleaning crew will have to wear fresh air masks.

Let's observe the men putting on these masks. Notice the face piece is placed under the chin first and then the rest of the face piece is pulled into place. First the lower straps are pulled up, and later the top ones are pulled up.

Now a test for leakage around the face piece is being made. The breathing hose is doubled and pinched shut while the wearer is instructed to inhale. No leaks being felt around the face piece while inhaling, the workman considers the masks safe.

Examining the breathing hose, we find that gaskets are in place at all joints. A tail rope is fastened to a "D" ring on the back of the harness. One man stands at the manhole constantly watching the men inside the tank and ready to pull them back to the manhole in an emergency.

Blower Kept to Windward

We also see that the fresh air blower is placed a safe distance from the manhole and on the windward side. This should prevent any possibility of recirculation of vapors that could build up a toxic condition within the mask. The man turning the blower has been instructed to never stop while men are in the tank. We can't help noticing that a pad has been provided over the edge of the manhole to protect the fresh air hose leading to the mask from becoming damaged.

Checking further, we find that all lines leading to and from the tank are blinded off—a good precaution against gas or oil seeping into the tank accidentally.

Now that the men have disturbed the sediment while shoveling, there is a possibility that additional gas will be liberated, and another vapor test is made. Finding that the vapor content has not increased appreciably, the safety engineer informs the tank cleaning foreman, and the men are directed to continue with the cleaning job.

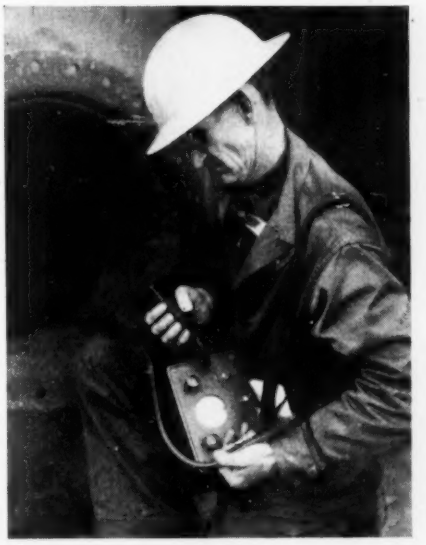
While observing this operation, we saw the foreman giving men directions to place signs warning truck and automobile drivers to keep a safe distance away from the tank and in this way eliminate a source of ignition. We also learn that all the crew has been trained to administer artificial respiration should circumstances at any time require it.

Having finished our inspection of this job, we work our way over to one in another tank farm. Here we find the tank cleaning crew already finished with the preliminary preparations. However, this time we notice a sign on the tank that reads—"Warning—This Tank Contained Leaded Gasoline." Observing closer we find instructions that read: "Do Not Enter Without Fresh Air Mask, Special Clothes, Rubber Boots, and Rubber Gloves." "Obtain special instructions from your department foreman before entering." This warning sign and the brief instructions mean that additional precautions will have to be taken.

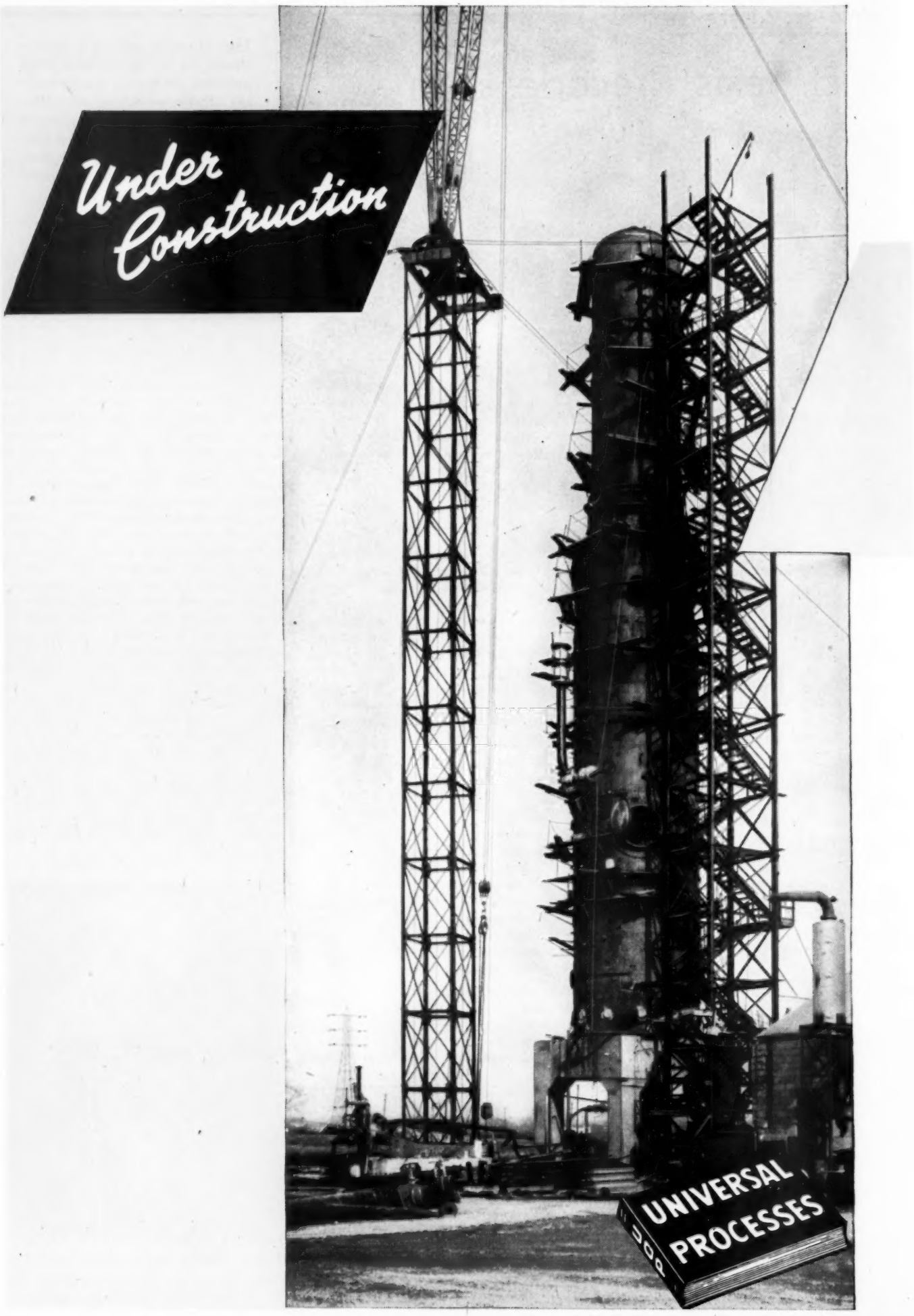
The foreman explains that his special instructions include rules that are laid down by the Ethyl Corp., requiring any person who enters a leaded gasoline tank that has not been thoroughly cleaned to wear a blower type or positive-pressure airline hose mask. Hose lines for air masks must be kept clean. If a workman notices any odor, as of gasoline, while wearing his mask, he must leave the tank at once and find the cause or get a new hose line.

All workmen must wear clean clothing from the skin out, also approved impermeable gloves and boots of good quality and in perfect condition. Clothing must be changed (and laundered) and a bath must be taken every day, either at the end of the day's work or when the job is finished. If at any time clothing gets soaked with gasoline or sludge, the workman must bathe at once and put on clean clothes.

Suspecting that the heavier vapors may lodge within the dike area especially on calm days, the foreman requests the safety engineer to make a gas test of the area. Finding no lurking vapor eliminates this suspicion and assures all concerned that conditions within the dike are safe for the work to proceed.



Utopia refinery safety engineer checks every tank with a petroleum vapor indicator before cleaning begins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Infrared Analyses of Alkylates

And Correlation of Alkylate Composition with Motor Tests

By GLENN M. WEBB and WILLIAM S. GALLAWAY
Universal Oil Products Co.

Methods have been developed in the laboratories of Universal Oil Products for analyzing alkylates by use of the infrared spectrometer. Briefly, the technique involves rough prefractionation of the sample into a series of cuts, followed by infrared absorption measurements on each cut.

As a result of this method, it is possible to make correlations between engine performance of and the composition of the individual hydrocarbons in an alkylate.

Details of the method employed and the calculations involved, with examples, are given in the following article, appearing exclusively in PETROLEUM PROCESSING. A later article will present data on the components of a group of HF and H_2SO_4 alkylates, as determined by this method, permitting quality comparisons betwen the alkylates produced with the two different types of catalyst.

IN THE past few years, the applications of infrared spectroscopy in the petroleum industry have broadened and increased tremendously from its use for only a few quite simple analyses, such as mixtures of iso and normal butane[1], to the study of nearly any type of sample, including plastics and synthetic rubber[2].

This paper will be concerned with the specific problem of the analysis of alkylates and the correlation of the results with engine tests. Not only is this problem of interest because of the use of alkylates in aviation fuels but the techniques can and have been carried over directly to the study of other complex mixtures of liquid hydrocarbons such as hydropolymers and straight run gasolines. For the basic principles of the infrared method, the reader is referred to the literature[3, 4, 5].

Procedure of Analysis

The general method used for analyzing typical C_4 alkylate, or any complex mixture of hydrocarbons, such as a straight run gasoline, consists in carrying out the following operations:

(1) Distill the sample carefully to break it up into a number of small components, each containing, if possible, not more than five fractions.

(2) Obtain the infrared spectrum of each of the cuts, or of a blend of the fractions if the distillation curve suggests it.

(3) Identify qualitatively the various hydrocarbons present.

(4) Calculate the composition in the manner to be described.

Details of each of these steps are as follows:

Distillation

The distillation step is carried out in a straight-forward manner in a column of good efficiency, such as a H. T. Podbielniak column. The volume charged is usually of the order of 200 ml. The collection system is designed so that the condensate is discharged directly to the surface of the liquid in the collecting burettes without contacting any stopcock grease enroute. The overhead rate and reflux ratio are adjusted so that a sharp separation is obtained between hydrocarbons, the boiling points of which differ by approximately 10° C., and so that the distillation is complete in a reasonable time, such as 6 to 8 hrs.

Attempts to attain more efficient distillation represent a considerable expenditure of extra effort and time with no appreciable gains in the *later* steps. The real gains made by the distillation are twofold. One is to limit the number of hydrocarbons present to five or less so the infrared analysis will be more easily made. The other is to separate those hydrocarbons which have their strongest characteristic lines at nearly the same wave length.

Thus, given reasonable separation, the important problem in the fractionation is to select proper cut points. To this end, the *idealized* distillation curve of Fig. 1 is presented, wherein the minimum number of good cut points are shown. These fractions will yield spectra showing the least interference between absorptions of the various components present. It would be very fortunate if exactly these points were selected, hence the usual technique is to take an excess number of cuts and then reblend after a careful study of the actual distillation plot.

It is wise to avoid making or reblending fractions in such a fashion that both ends of any plateau are included in one sample. Also, one should not make large cuts which include one end of the plateau. The former precaution will increase the reliability of the analyses since often the next lower and next higher boiling compounds have somewhat similar spectra. The latter will increase the accuracy by precluding the possibility of missing small amounts of the next higher boiling material in a relatively large cut.

Infrared Absorption Spectra

The authors have recorded the spectra of the samples on a large Gaertner spectrometer having rock salt optics similar to the one described by McAlister[6]. Any infrared spectrometer would be satisfactory, provided it possessed the required high resolution and was equipped to give a continuous recording from which the transmission of the sample at any wave length could be measured and reproduced to at least ½%. Typical slit widths, i.e., resolving power, are given in Table 1. In any case, the instrument should be operated at maximum resolving power consistent with stability and reproducibility of the recordings.

The spectral interval scanned should be from 7.5 to 15 microns. While many samples can be analyzed satisfactorily using only the range from 7.5 to 11μ, it is not good practice so to limit the wave

TABLE 1—Typical Slit Widths

Wave Length (Microns)	Effective Slit Width (Microns)
7.5	0.02
10.0	0.03
12.5	0.05

length interval, since some useful and often necessary information will be missed. Since the complete recording requires only one-half hour, the time saved is not of importance.

The samples are placed in a cell for liquids which follows the design of Gildart and Wright[7]. This type is of advantage since it is readily cleaned, refilled, and does not use any waxes or cements. It will easily retain any hydrocarbon which is normally liquid at room temperature. For paraffinic samples, a liquid film of 0.1 mm. is quite satisfactory.

Qualitative Identification

At this point in the analysis, past experience is of great assistance, i.e., one knows more or less what compounds to look for in each sample. In the case of alkylates, only those materials given in Tables 2 and 3 are usually found. The further restriction on the composition induced by the distillation reduces the number of materials possibly present to a very few. The actual identification is made by a direct comparison of the sample recording with those of the pure hydrocarbons.

Fig. 2 shows such a comparison between the spectrum of a synthetic blend of three hydrocarbons which all boil very close to 80° C. It takes but a moment to see that all the absorption lines of each of the pures are reproduced (though reduced in intensity) in the sample and further that no lines are found in the spectrum of the sample which are not accounted for by those of the pure hydrocarbons. The qualitative identification is thus complete.

It might be well to point out here that certain wave lengths can be used to exclude certain types of structure. As an example, the absence of an absorption line at 8.9 microns shows that there is no material present such as 2,3-dimethylbutane or 2,3-dimethylpentane.

It is at this stage in the problem that the use of continuously recorded spectra is superior to merely measuring the transmission of the samples at those wave lengths where the absorption is characteristic of the suspected components. Not only are the later calculations simplified since one needs to calculate only those materials actually found to be present, but one has a safeguard against the unexpected. A little acetone left in after cleaning the sample burettes will be quickly spotted and correctly allowed for. Occasionally, some olefinic material will be found and even accidental mislabeling or misblending of cuts will occur. In addition, one can also select for each sample the best absorptions to use as a measure of the amounts of the various components.

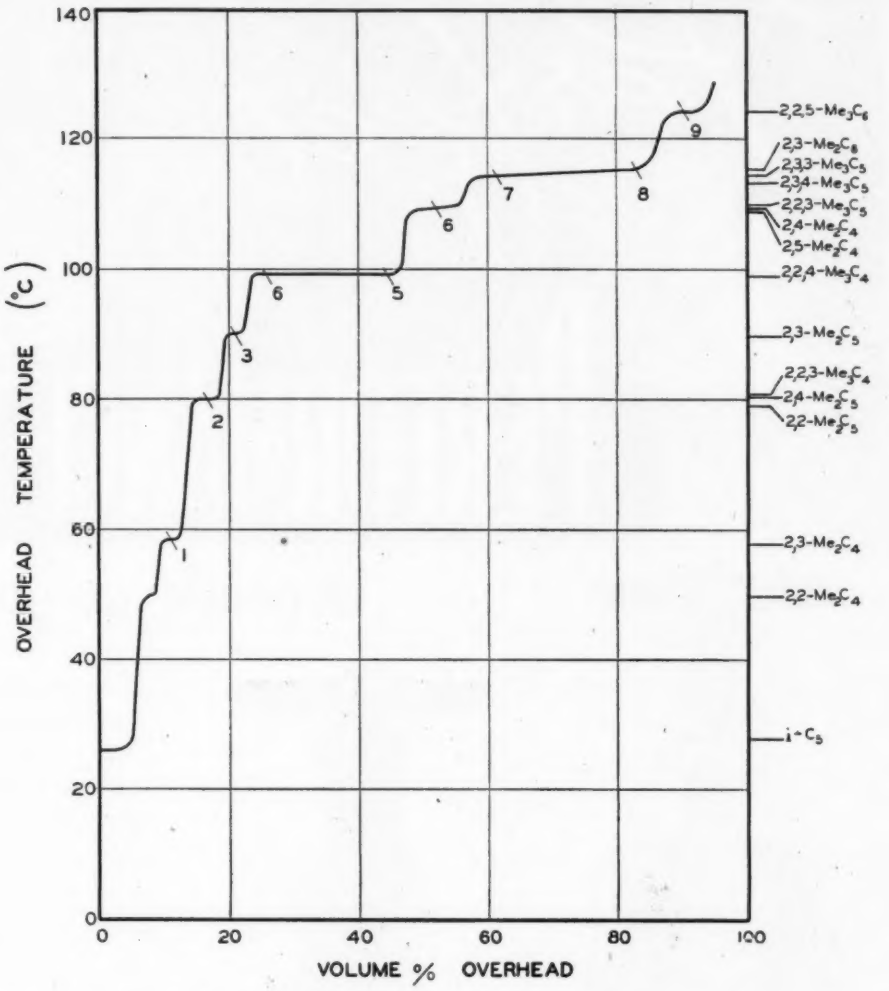


Fig. 1—Idealized distillation curve of a C_4 alkylate. Numbered points indicate minimum number of good cut points

Theory of Calculations

Infrared analyses are based on the assumption that Beer's law holds both with respect to concentration of a given material and additivity of the absorption of each component of the mixture. This statement is equivalent to the following equation which holds for a given wave length and a given cell.

$$D = \log 1/T = ax + by + cz + \ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

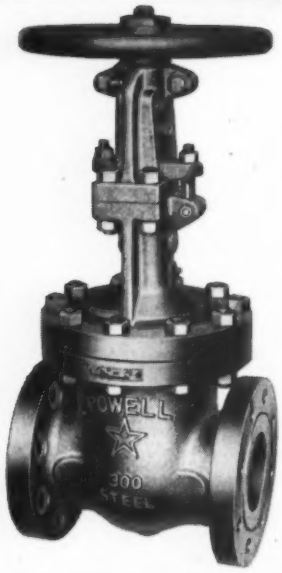
D = Optical density,
T = Transmission of sample,
$a, b, c,$ = Constants,
$x, y, z,$ = Concentraticin of the component.

It is easy to see that if a is large and all other constants are small, the optical density at this wave length is a good

TABLE 2—Optical Densities (x 1000) of Pure Hydrocarbons (For Alkylate Analysis)

Wave Length (Microns)	i-C_5	2, 2-Me_2C_4	2, 3-Me_2C_4	2, 2-Me_2C_5	2, 2, 3-Me_3C_4	2, 4-Me_2C_5	2, 3-Me_2C_5	2, 2, 4-Me_3C_5
10.28	705	85	85					
13.08	530	40	5					
8.21	55	1620	60	440	985	70		
12.77	135	540	10	40	5	10		
8.87	125	25	1610	30	115	75		
9.64	170	85	865	40	25	25		
8.27		530	60	1280	1060	75	69	980
13.50		15	15	670	0	0	90	15
9.04		40	125	70	940	40	145	85
9.22		205	75	50	1350	50	95	40
8.54		35	195	65	420	1430	240	840
10.15		310	210	45	80	607	380	335
12.35		25	0	20	15	355	75	30
8.91				30	130	60	1265	65
10.37				70	70	60	625	90
7.99				1090	300	105	180	1020
8.28				1280	1060	75	65	1110
8.53				65	400	1200	230	905

depends on *perfect* control.



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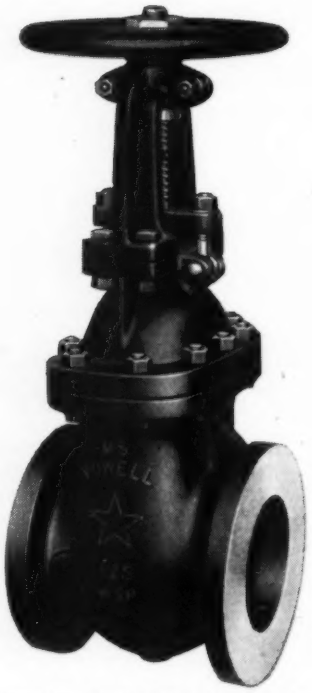

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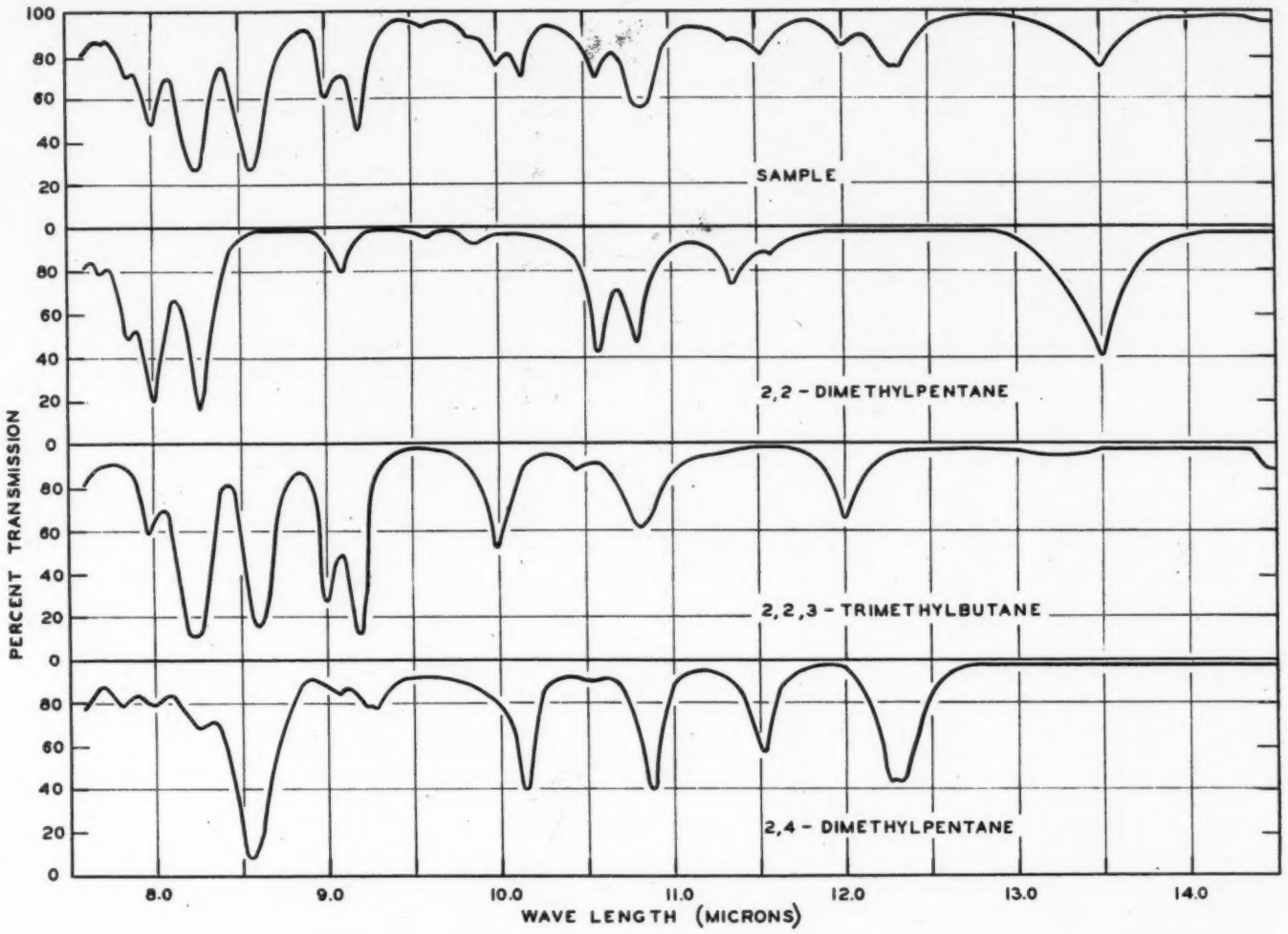

Fig. 2—Comparison of sample spectrum with spectra of pure hydrocarbons

measure of the concentration of the material given by x. The solution of a series of such equations for different wave lengths, one for each material, yields the desired composition.

Instrument Calibration

The calibration consists of first selecting those wave lengths at which a given pure material exhibits high absorption and other reasonably close boiling materials do not. The choice is made by a visual inspection of the spectra of pure hydrocarbons. Several points should be selected for each compound to guard against possible interference by other materials.

The second step is to obtain the constants of Equation 1 given above. These numbers (a, b, c) are simply the optical densities of the pure materials at the selected wave lengths and are obtained by determining the transmission from the recordings. A representative set of these numbers is given in Tables 2 and 3 for those hydrocarbons normally encountered in alkylates. As an example, according to line 1 of Table 1, if there is a mixture of the first three compounds given in this table in concentrations of x, y, and z respectively, the optical density of this sample at 10.28 microns will be

$$1000\,D = 705x + 85y + 85z \quad \ldots\ldots (2)$$

The use of the factor of 1000 is merely for the sake of convenience in eliminating decimal points when using a slide rule to calculate the logarithms.

If no changes in the cell take place, these calibration tables should remain constant indefinitely. However, the use of the cell does cause some variation in the window transparency and thickness of the inner space. Changes in the window transparency affect only the calculation of the per cent transmission of the sample; thus, periodic recordings of a blank cell will give the necessary data. It is actually superior, here, to use a highly transparent material such as CS_2 to determine the 100% transmission curve, since reflection

TABLE 3—Optical Densities (x 1000) of Pure Hydrocarbons (For Alkylate Analysis)

Wave Length (Microns)	2, 2, 4-Me_3C_5	2, 2-Me_2C_6	2, 5-Me_2C_6	2, 4-Me_2C_6	2, 2, 3-Me_3C_5	2, 3, 4-Me_3C_5	2, 3, 3-Me_3C_5	2, 3-Me_2C_6	3, 4-Me_2C_6	2, 2, 5-Me_3C_6
7.99	**1020**	825	145	85	465	60				
8.28	**1110**	585	110	70	760	95				
11.18	20	**525**	30	60	55	225	75			
13.71	20	**605**	70	40	50	25	5			
13.29	20	90	**490**	75	30	105	50	135		
10.30	250	145	80	**650**	455	260	75	260		
13.03	15	80	190	**485**	275	50	210	140		
9.25	35	75	155	140	**795**	105	255	50		
12.83	20	130	70	145	**590**	15	590	125		
8.90	60	70	60	95	130	**1850**	135	970	450	255
9.61	25	25	195	130	85	**950**	240	210	105	50
9.20		105	275	115	250	100	**890**	40	75	70
9.93		100	35	240	250	245	**1310**	245	640	15
13.51			175	35	10	15	15	**450**	150	85
10.54						75	75	230	**700**	70
7.99						60	150	180	145	**910**

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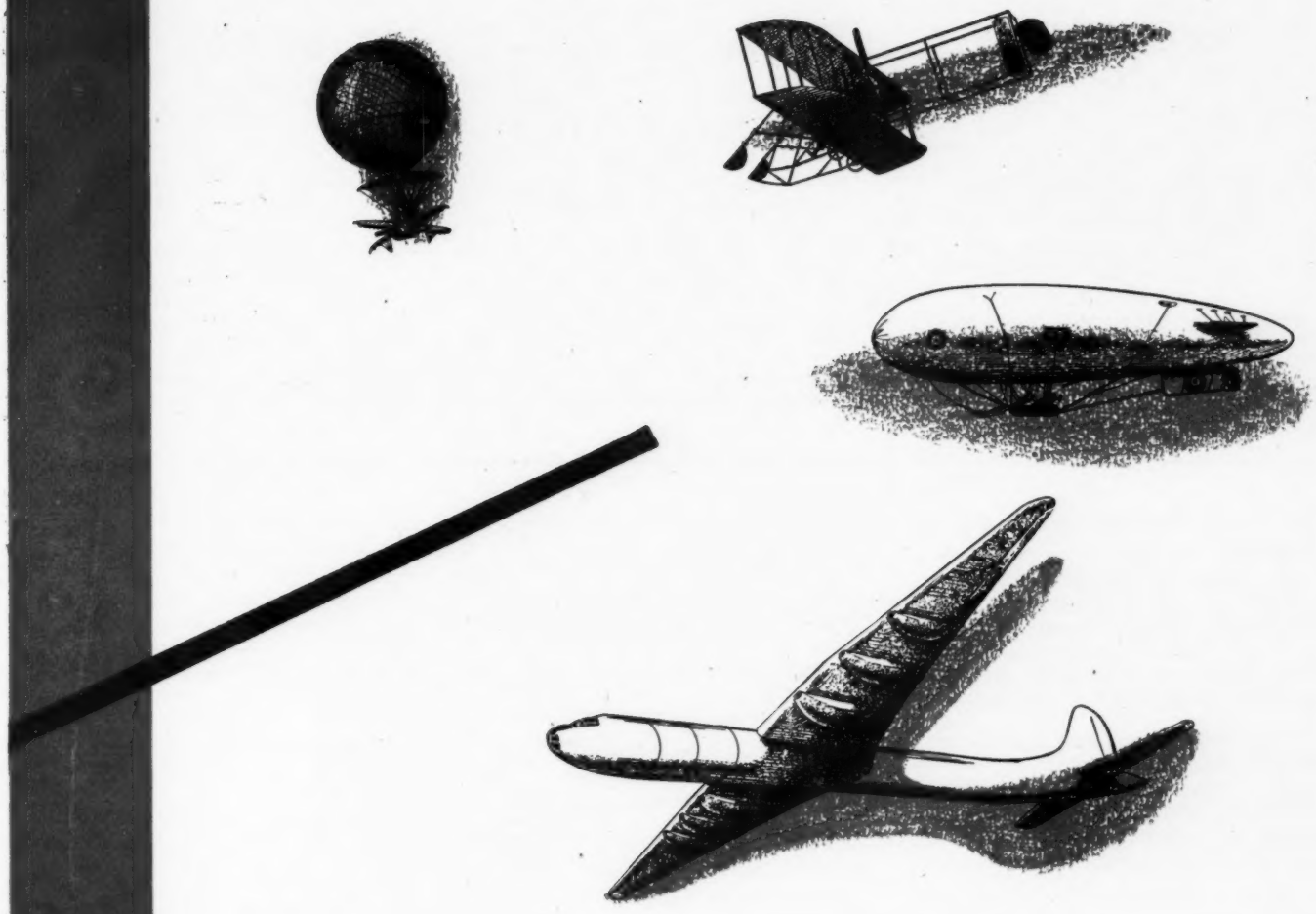

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TABLE 4—Typical Completed Analysis of an Alkylate (1331-119)

Cut No.	Cut Temp.,[a] °C	Cut Vol.	1-C_5	2, 3-Me_2C_4	2, 4-Me_2C_5	2, 3-Me_2C_5	2, 2, 4-Me_3C_5	2, 5-Me_2C_6	2, 4-Me_2C_6	2, 2, 3-Me_3C_5	2, 3, 4-Me_3C_5	2, 3, 3-Me_3C_5	2, 3-Me_2C_6	C_9+
1	1-52	3.3	35	57	8	..	..	..	..	..	..	..	..	..
2	52-78	3.2	..	23	77	..	..	..	..	..	..	..	..	..
3	78-94	3.1	..	..	42	29	29	..	..	..	..	..	..	..
4	94-98	3.2	..	..	10	9	81	..	..	..	..	..	..	..
5-11	98	44.7	..	..	..	..	100[b]	..	..	..	..	..	..	..
12	98-106	6.5	..	..	..	..	81	11	5	2	1	..	..	..
13	106-110	6.2	..	..	..	..	4	44	23	8	21	..	..	..
14	110-112	6.1	..	..	..	..	..	18	11	2	53	16	..	..
15	112-114	7.2	..	..	..	..	..	..	..	..	62	36	2	..
16	114	5.8	..	..	..	..	..	..	..	..	50	43	7	..
17	114-116	2.8	..	..	..	..	..	..	..	.	36	49	15	..
Botts	.....	7.9	..	..	..	..	..	..	..	..	..	14	6	80
Composition based on Total Sample			1.2	2.6	4.3	1.2	53.7	4.6	2.4	0.7	13.0	8.6	1.4	6.3

(a) Cut temperatures of 1st four fractions not taken, normally due to small volume of original sample. Barometric Pressure=740 mm.
(b) Cuts 6-10 inclusive, not run since 5 and 11 were 100% 2, 2, 4-trimethylpentane.

losses at the inner faces of the cell are eliminated.

Any change in thickness of liquid film is determined by recording a sample of known optical density. Correction for any variation is made by a proportional change in all the figures of the calibration table since D is proportional to cell thickness.

Under normal conditions, a cell should remain unaffected by its use for several hundred samples. If a new cell is put in service, one proceeds as if only the transparency and cell thickness of the old one have changed. Thus it is not necessary to repeat all the original calibration work.

Unfortunately, the data presented in Tables 2 and 3 are not transferable from one spectrometer to another, since the optical densities are somewhat sensitive to the operating conditions of the instrument and to the quality of the optics and their adjustment. Thus, one must be careful that the unknown samples are run under the same conditions as the pure materials.

Calculation of Sample Composition

The best procedure for presenting the method of calculating the exact composition is to follow through a specific example. Assume that in the particular sample in question only isopentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are identified. That is to say, all the absorptions found in the sample pattern are accounted for by the presence of these three materials. An inspection of Table 2 shows the wave lengths of 10.28, 8.21, and 8.87 microns to be satisfactory points at which to measure. At these points, it is found directly from the sample recording that the transmissions are 46.5, 41.0, and 16.5%. We then get the following by use of a slide rule. Again, the figure of 1000 is for convenience only, since it eliminates decimal points.

$$D_1 = 1000 \log 1/.465 = 332$$
$$D_2 = 1000 \log 1/.410 = 388$$
$$D_3 = 1000 \log 1/.165 = 779$$

Since the numbers given in Table II are the constants of the desired equation, we have

$$332 = 705x + 85y + 85z$$
$$388 = 55x + 1620y + 60z$$
$$779 = 125x + 25y + 1610z$$

where x, y, z are the desired concentrations of isopentane, 2,2- and 2,3-dimethylbutane, respectively.

The solution is obtained by standard methods of approximation. After rewriting the equation as given below, assume first that $y = z = 0$ and calculate x.

$$x = (332 - 85y - 85z)/705$$
$$y = (388 - 55x - 60z)/1620$$
$$z = (779 - 125x - 25y)/1610$$

Use this value of x with $z = 0$ to get y.

Then get z.

$$x = 332/705 = 47\%$$
$$y = [388 - (55 \times 47\%)] / 1620 = (388 - 22)/1620 = 22\%$$
$$z = [799 - (125 \times 47\%) - (25 \times 22\%)]/1610 = (799 - 59 - 5)/1610 = 44\%$$

Repeating the process using these first

Dr. Glenn M. Webb, director of the Physics Division of Universal Oil Products Co., graduated from California Institute of Technology in 1931 with B.S. degrees in physics and mathematics. Postgraduate work in the same subjects at Washington University, St. Louis, earned him the M.S. degree in 1933 and the Ph.D. degree in 1935.

Dr. Webb

From 1935-37 he was research physicist at Western Cartridge Co., East Alton, Ill., joining U.O.P. in 1937. For a year and a half during the war Dr. Webb, in addition to his work at Universal, was engaged as a consultant on catalysts in the Manhattan atomic bomb project.

Dr. Gallaway

Dr. William S. Gallaway, research physicist with U.O.P., is a specialist in infrared spectroscopy. He was educated at Lehigh University, George Washington University, Pennsylvania State College and University of Michigan, completing postgraduate work at the latter university in 1941 with the Ph.D. degree in physics. Dr. Gallaway was a teaching assistant at three of the above schools before joining Universal in 1941.

approximate values will yield results closer to the correct values.

$$x = [332 - (85 \times 22\%) - (85 \times 44\%)]/705$$
$$= (332 - 19 - 37)/705 = 39\%$$
$$y = [388 - (55 \times 39\%) - (60 \times 44\%)]/1620$$
$$= (388 - 22 - 36)/1620 = 21\%$$
$$z = [779 - (125 \times 39\%) - (25 \times 21\%)]/1610$$
$$= (779 - 49 - 5)/1610 = 45\%$$

It is easily seen that a third calculation is not necessary since the values will repeat to within 1%. It is rarely necessary to proceed beyond this point. In actual practice, much of the foregoing writing is omitted, thereby saving considerable time. Also, a reasonable guess of the composition from a visual inspection of the records can be used for the first approximation, and the correct results may be obtained with the first calculation.

The failure of the calculated composition to total to 100% is due to the deviations from Beer's law. The error is a maximum near 50%, hence the corrections are based from this point, i.e., 60% and 40% are corrected equally. Since, in our example, all the values are below 50%, they are reduced proportionately to 37, 20, and 43% respectively. Further details of the method of calculation may be found in Brattain's paper on C_4 hydrocarbon analysis[5]. There one will also find a satisfactory method for correcting for stray light.

It is always wise before proceeding to the next cut to check for the next higher, or lower, boiling materials or for any compound, the absence of which is questionable. To do this, calculate, from the composition found, the optical density at the proper wave length and compare with the value determined from the sample record. Failure to check is an indication of a component that was overlooked.

The total time of analysis is approximately 30 min. for the instrument work and 10 min. for the calculations per fraction. If an appreciable number of samples having the same components are expected, some saving in calculating time is effected by inverting the equations from the form

$$D_1 = ax + by + \ldots$$

to

$$x = mD_1 + nD_2 + \ldots$$

as described by P. D. Crout[8].

The repeatability of the results is indicated by the fact that check runs on a known blend made over a period of three months showed a maximum spread between highest and lowest values of 2.5% with an average deviation of ½%. The reliability is also obtained from the same data which show the deviations from the known values to average somewhat over ½%.

A typical completed analysis is given in Table 4. In this case, because of the small volume of the original sample, the first four cuts were not made at the usual points. However, since the alkylate was made under rather mild conditions, no 2- or 3-methyl types of hydrocarbons were encountered and the analyses of the early fractions were made without difficulty. The cuts boiling above 100° C. show poorer separation by distillation than normal, which is probably also due to the small sample charged to the fractionating column. The example does show, though, that a very satisfactory result can be obtained under adverse conditions.

More to Come

A second article by these same authors will appear in an early issue of PETROLEUM PROCESSING and will present the results of studies on various alkylates made using the infrared spectrometer method described above.

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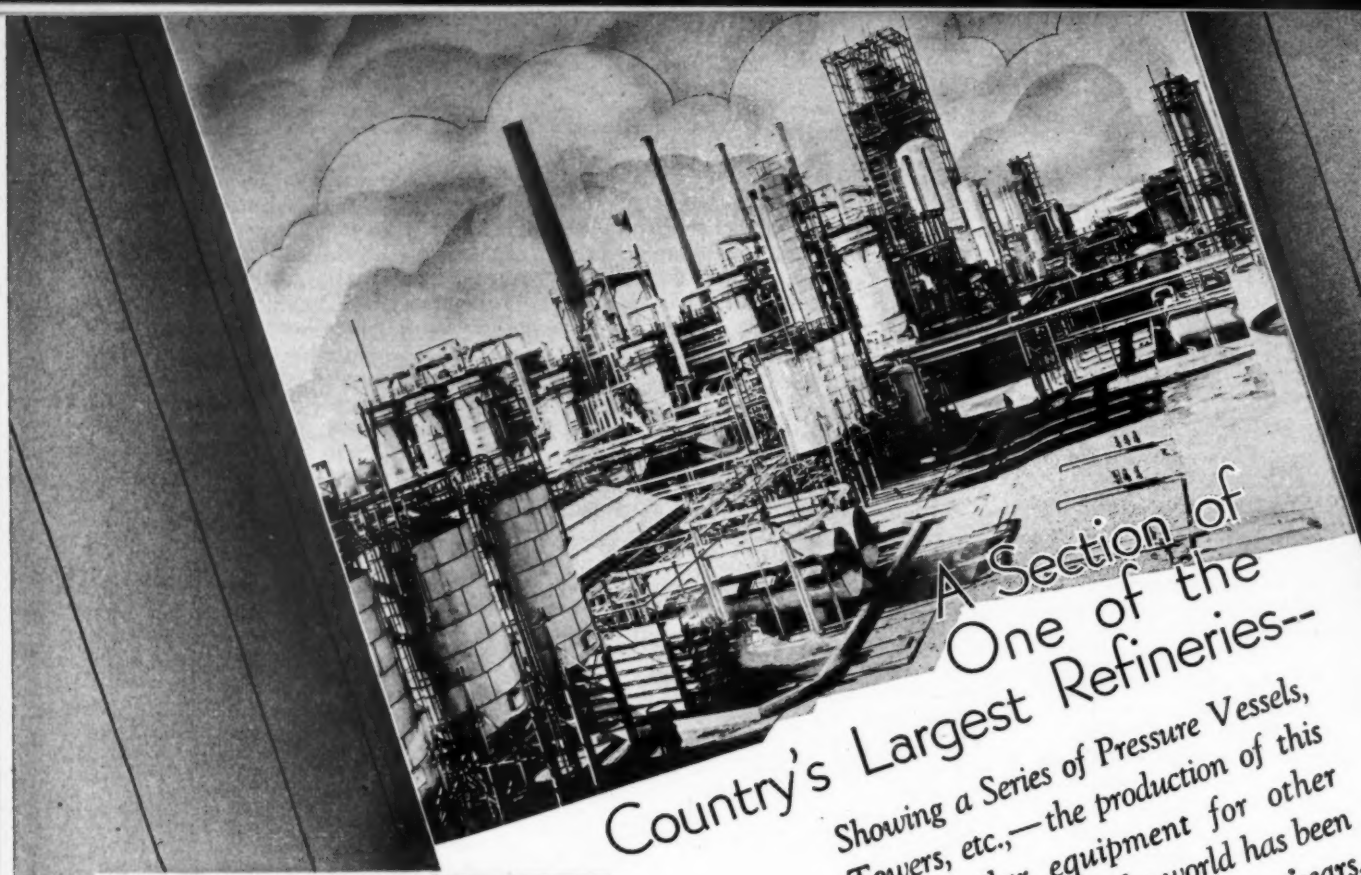
Infrared absorption spectrometer of the type used by Universal's physicists to analyze alkylates. The operator shown in this picture is Dr. William S. Gallaway, co-author of the present article



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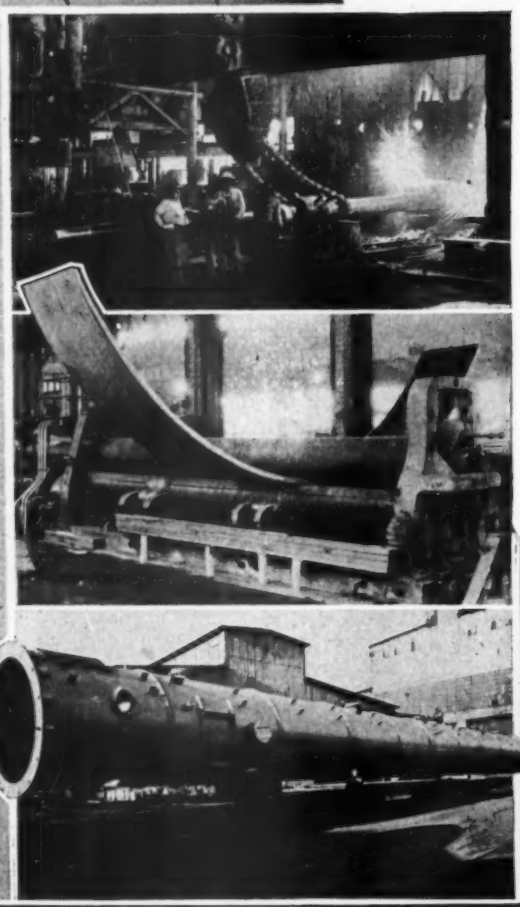

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Automatic Control of Processing Is Product Quality Insurance

Modern refineries are dependent to a high degree on automatic control instruments for the efficient operation of processing units to manufacture products of the quality required. The installation in refineries of the conventional instruments for measurement of flow, temperatures, pressures and liquid levels is described, also of air-operated controllers. The application of instruments in conducting tests on processing units as well as in following their day-to-day performance is presented briefly.

By ROBERT H. WEHRLE
Mechanical Engineer
Standard Oil Co. (Ohio)

THE quality of petroleum products and the efficiency of operating units in the refinery are dependent in a large degree on the performance of automatic control instruments. The correct end point, the maximum cracking yield or the optimum catalytic conversion is obtained only when temperatures and pressures are held within narrow limits. A few years ago such limits would have been considered unattainable but are now maintained month after month by modern type instruments.

The purpose of this article is to describe briefly the various types of instruments which are commonly used in the refinery and to illustrate how they are applied to processing units.

Flow Measurement

Flow measurement is essential to the refinery operating department in determining the rate at which they are operating their units. It is also very important to the Technical Service Section not only in following the day-to-day performance of the refinery but also in conducting a test on a process unit. Material balances and heat balances are both dependent on the measurement of flow rates and, unless these measurements are accurate, the test work which has been done is of little value.

Differential Meter

Practically all flow measurement within the refineries is made by means of the differential meter. This type of meter is used in conjunction with a primary device such as an orifice plate, flow nozzle or venturi tube installed in the pipe line where the flow is to be measured. Since the velocity of the flowing fluid varies as the square root of the pressure differential between a point upstream of this orifice or primary device and one downstream of it, it is possible to calculate accurately the velocity, providing we have a suitable instrument for measuring this differential pressure.

The conventional instrument which performs this function is essentially a U-tube having one leg of the U connected into the pipe line on the upstream side of the orifice and the other leg connected into the downstream side. The lower portion of the U-tube contains a quantity of mercury. Any differential pressure across the orifice will be indicated by a rise of the mercury column in the low pressure leg with a corresponding drop in the high pressure leg. A float installed in one of the legs of the U-tube is connected by means of levers so as to position a pen arm which traces a record on a clock-driven chart, thus plotting a graph of differential pressure against time.

It is the usual practice in the refinery to use a meter chart called a "square root" chart. The advantage of using this type of chart is that the operator can determine directly the rate of flow without having to give any thought to the fact that the flow varies as the square root of the differential pressure. Knowing the "chart factor" he can compute the flow rate by simply multiplying this factor by the chart reading.

An explanation probably should be given here of the terms "chart factor" and "maximum flow". The "maximum flow" is that quantity of liquid which when flowing through the chosen orifice will create a differential pressure equal to 100% of the range of the meter. The "chart factor" represents a quantity which is 10% of the "maximum flow". Thus, the reading on the chart multiplied by the "chart factor" gives the rate of flow since the divisions on the chart are numbered 0 to 10.

The majority of the refinery meters have a differential pressure range of 0 to 100 in. of water but there are numerous meters having ranges other than this. It is, therefore, necessary to determine the range of the meter as well as the orifice and pipe diameter if it is desired to calculate the "maximum flow" or "chart factor".

Differential Pressure Taps

It has been the usual practice in our refineries to install the orifice plate between a pair of special pipe flanges which are known as orifice flanges. Each of these flanges has a hole drilled radially through it which serves as a pressure tap for the meter. This hole is drilled in such a manner that its center will be 1 in. from the face of the orifice when the latter is installed in the line. When the differential pressure taps are so located they are referred to as "flange taps".

There are two other methods of locating the differential pressure taps, known as "Vena Contracta taps" and "pipe taps". Where "Vena Contracta taps" are used the high pressure tap is located 1 pipe diameter upstream from the orifice and the low pressure tap at the Vena Contracta. With "pipe taps" the high pressure tap is located 2½ pipe diameters upstream from the orifice plate and the low pressure tap 8 pipe diameters downstream from the plate.

The following information should be included with the data on any test of a process unit where flow rates are to be calculated.

1. Meter reading
2. Differential range of meter
3. Orifice diameter
4. I.D. of pipe or nominal diameter together with weight or schedule of pipe
5. Location of differential pressure taps
6. Density of fluid in meter leads
7. Static pressure at orifice
8. Temperature of fluid being measured
9. Specific or API gravity of fluid being measured
10. Character of fluid being measured

The last four items are used to determine the density of the fluid at the point

Bourdon tube type pressure controller with a range from 15 psig to 30 in. mercury vacuum. This instrument is used to control cat-cracker evacuation equipment

where it is flowing through the orifice. It is necessary to make this determination as the differential pressure across the orifice varies as the square root of the fluid density for a given flow. These last four items of data can also be used to determine the viscosity of the fluid at the flowing conditions.

Most orifice meter applications in the refinery are on fluids which are relatively non-viscous at the temperature at which they are measured. Inasmuch as the viscosity correction is usually less than 1% on such fluids, the viscosity factor is often not included in the orifice calculation.

The density of the fluid in the meter leads should be noted in the test data, as frequently a sealing fluid is used in the piping between the orifice taps and the meter body which does not have the same specific gravity as the fluid being measured. The sealing fluid on many installations is a solution of 50% Permaguard (ethylene glycol) and 50% water. This solution has a specific gravity of 1.125.

The temperature data are used not only to calculate the density of the flowing fluid, but also to determine the extent to which the area of the orifice opening has increased due to thermal expansion.

Orifice meter readings on smooth, non-pulsating streams will normally be accurate within 1% of the maximum flow of the meter providing the equipment is properly installed and maintained. Disturbances upstream of an orifice such as valves or fittings can affect the accuracy of the meter and standards have been established for the minimum length of straight pipe upstream of the orifice for various fittings and combinations of fittings.

The condition of the orifice plate is an important factor, especially the upstream edge, which must be sharp and free from nicks or burrs. The density of the fluid in the meter piping leading from the pressure taps at the orifice to the meter body should be uniform so that the head of fluid in the one lead will balance in the other lead.

Finally, the meter body should be in accurate calibration and free from any friction in its moving parts. If attention has been given the above mentioned factors, consistently accurate flow measurement can be obtained from the orifice type flow meter.

Pressure Measurement

A refinery process unit normally has more pressure instruments including indicating pressure gauges than any other classification of instrumentation. Any distillation unit, working at pressures above or below atmospheric, must have these pressures accurately measured and controlled if temperature regulation is to be of any value in obtaining proper product specifications. In addition to the instrumentation on the distillation equipment, pressure gauges will be found on practically every pump discharge and numerous recording or control instruments are installed on the fuel gas and steam lines throughout the plant.

Internal Mechanism

The 6-in. diameter or smaller indicating pressure gauge normally contains a Bourdon tube which through a system of linkages and gears positions the indicating pointer to correspond to the pressure imposed upon the tube. Gauges to be used on steam or air lines are purchased with bronze Bourdon tubes whereas those for gas or oil lines are supplied with steel tubes for safety reasons in case of fire.

The 10 or 12-in. diameter recording or controlling instruments utilize spirals, helices, Bourdon tubes or spring and bellows diaphragms, depending primarily on the maximum pressure to be measured. For pressures of more than 20 psig and less than 4000 psig most instruments are supplied with either a helical or spiral type of element. The spring and metallic bellows element is normally used for measurements of pressures less than 20 psig.

The relationship between pressure and linear movement is far superior with the spring and metallic bellows than with the other types of elements. Furthermore the power available to position the recording pen or pointer is much greater with the bellows type.

The pressure to be measured is often that existing in an elevated pipe line or pressure vessel. In order to facilitate the reading of such a pressure while standing at ground level, the gauge is mounted at eye level and the pressure piping extended from the pipe line down to the gauge.

If the fluid in the pipe line is a liquid, wet gas, or steam, the connecting piping between the pipe line and the gauge will probably be filled with liquid. This head of liquid will exert a pressure on the gauge element which will cause the gauge to register a higher reading than actually exists within the pipe line or vessel unless the gauge has been compensated for this head of liquid. The increase in pressure created by this difference in elevation amounts to 0.4335 psi for each foot of head for a liquid having a specific gravity of one and is proportionately less for liquids of lower specific gravity.

Temperature Measurement

Temperature measurement, essential as it is to distillation operations, is probably even more important in the protection of refinery equipment. The refinery operators are continually checking the temperatures of furnace tubes, catalyst cases, engine jackets, turbine and motor bearings, in addition to furnace outlet and tower temperatures to insure the safe operation of their equipment.

The familiar mercury-in-glass thermometer is used in a great many applications within the laboratory, but its use on process equipment is limited due to the fact that it is so easily broken. In its place are used either the thermocouple-potentiometer system or the pressure type temperature measuring instrument often referred to as the capillary thermometer type.

The actuating element of this latter type of instrument is either a helix, a spiral, or a Bourdon tube similar to that used in the measurement of pressure. This element which serves to position the recording pen or indicating pointer is mounted in the instrument case and is connected by means of capillary tubing to the thermometer bulb. The latter is normally installed in a socket or thermowell which is in contact with the fluid, the temperature of which it is desired to measure.

Pressure Type Thermometers

The thermometer system (including the bulb, capillary tubing and actuating element) is classified primarily according to the type fluid with which it is filled. The following are the classifications which the manufacturers have given to various types.

Class 1 is known as the partially compensated liquid-filled system. It is based on the volumetric expansion of a liquid with temperature and uses an evenly graduated chart. The instrument is partially compensated, which means that the case is compensated for changes in ambient temperature. That is, the ambient

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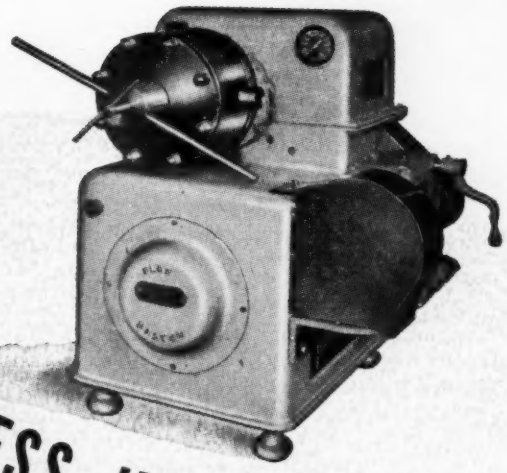

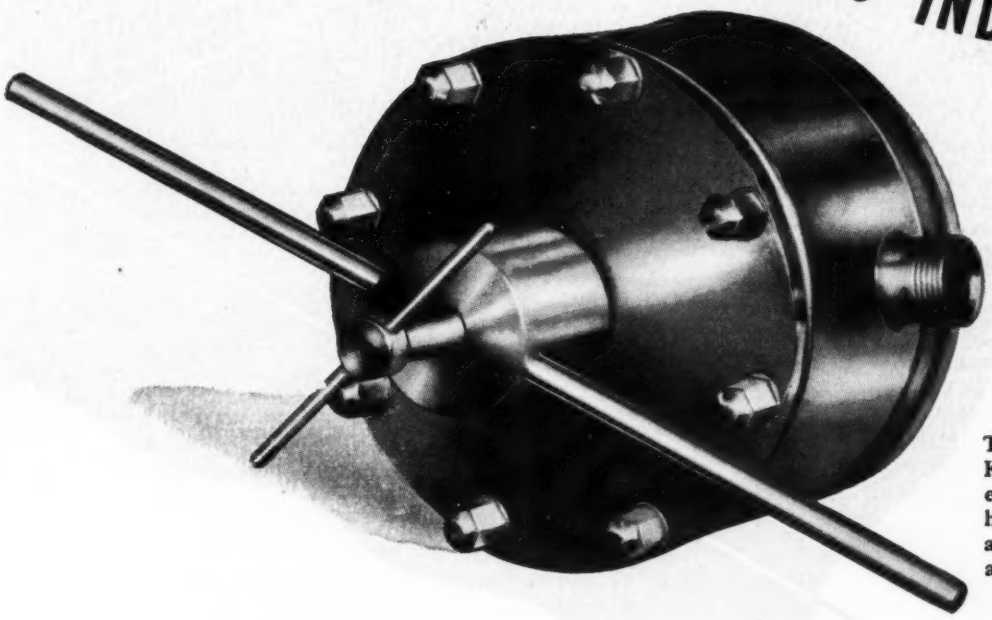

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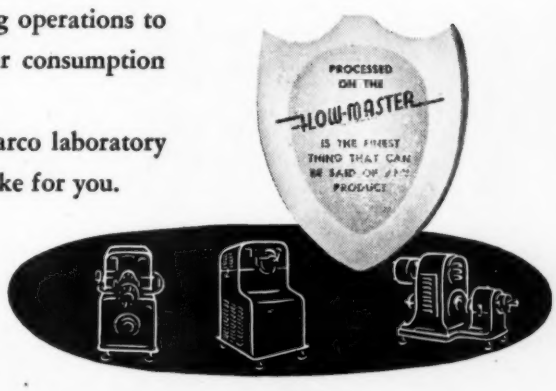

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temperature may vary from 0 to 100° F. without affecting the reading of the thermometer, provided both the case and the tubing are exposed to the some temperature.

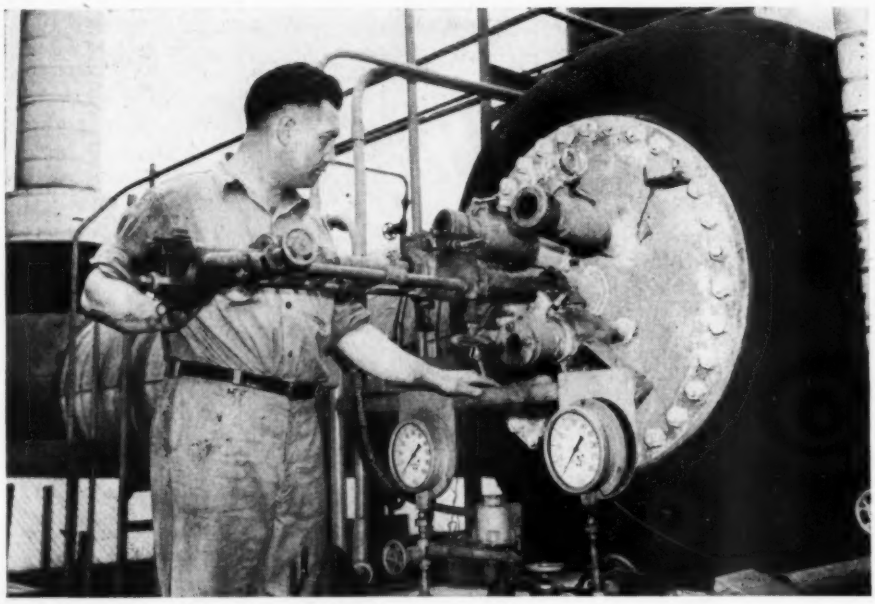
Class 2 is known as the vapor-tension system. A change in temperature causes an increase in vapor pressure of the special filling liquids which are used, such as alcohol, ether, methyl chloride, sulfur dioxide, toluol, or hexane. It is not a straight-line function and, therefore, the chart or scale is unequally divided, the divisions increasing in width as the temperature rises.

Advantage is Rapid Response

One advantage of this class of instrument is that it is very rapid in response to changes in temperature; furthermore, it requires no compensation due to variations in ambient temperature of the case or capillary tubing. However, if the temperature to be measured goes both above and below the case temperature and the case and bulb are at different levels, the Class 2 instrument should not be used. The temperature limits are—25° F. to 600° F.

Class 3 is known as the gas filled system. It is based on the volumetric expansion of inert gases in accordance with the gas laws, with subsequent increase in pressure. It has a straight-line function, with evenly graduated charts. The disadvantage of this type is the fact that the bulbs are rather large resulting in a slow response to temperature change. Compensation for temperature changes along the tubing is obtained by increasing the bulb size. The temperature limits are from —100° F. to 1000° F.

Class 4 is the fully compensated liquid filled system. It is similar to Class 1 instruments except for the fact that the capillary can be at a different temperature from that of the case and no error will be introduced into the reading.



Two 300 psi direct pressure gages on the fuel line to an oil-burning turbo-charger. The indicating pointer is actuated by a Bourdon tube

Brown Instrument Co. and Foxboro Co. compensate their Class 4 instruments by incorporating two capillary tubes and two spiral or helical actuating elements. The measuring spiral is connected to the bulb through its capillary in the usual manner. The compensating spiral is connected to its spiral which is dead-ended at the bulb. The two spirals expand in opposite directions and are connected directly to the pen shaft. A change in temperature within the instrument case or at points along the capillary will affect both actuating spirals to the same degree and the results will exactly neutralize each other.

Taylor does not use the dual system of capillaries and actuating elements in order to compensate for temperature variations of the case or capillary. They obtain true temperature readings by inserting within the bore of the tubing a special alloy wire with a coefficient of expansion so related to that of the tubing and mercury that any expansion or contraction of tubing and mercury, due to fluctuating temperatures between bulb and recorder, is compensated by a change in the volume occupied by the alloy wire at the point of fluctuation.

The temperature limitations on this class of instruments vary with the manufacturer. One offers this instrument for temperatures as low as —100° F. but limits the maximum temperature to 500° F. Another manufacturer offers operating ranges with limits of —40° F. to 1200° F.

Thermocouple-Potentiometer Systems

The thermocouple - potentiometer is based on the well-known principle that a small electromotive force will be generated by two dissimilar wires properly welded together at the ends, when one junction is at a higher temperature than the other. Such a sensitive element, made of two dissimilar metals, either pure or alloy, is known as a thermocouple. The fused end is known as the "hot junction" and is placed at the point where the temperature is measured; the free ends are carried through suitable leads to the emf detecting system, which point is known as the "cold junction."

When the hot junction is heated, the millivoltage generated is proportional to the temperature and the scale on the measuring instrument can easily be calibrated as a temperature scale. Although the emf (electromotive force) generated is great enough to permit direct deflection of a galvanometer pointer whose scale is calibrated in degrees, the most widely used method is the potentiometer system in which the emf generated is balanced with a known emf across a potentiometer circuit.

The first method is known as the millivoltmeter system, and, although quite satisfactory from a point of view of accuracy for many applications, nevertheless is subject to errors greater than the refining industry can tolerate.

One important feature incorporated in the potentiometer method is that the length (resistance) of extension leads from the thermocouple to the recording or indicating instrument does not affect the accuacy of the reading, whereas, in the millivolt system, the recorder must be recalibrated if any great changes are made in external resistance.

The emf generated in a thermocouple system is dependent not only on the tem-

The instruments at upper center and upper right are temperature recorders and controllers of the potentiometric type for a pair of butane tower reboilers. Temperature is detected by an iron-constantan thermocouple and is recorded in degrees F.

perature of the hot junction but also on that of the cold junction. Frequently, when temperature measurements are made in the laboratory the cold junction is held at 32° F. by immersing the wires in a mixture of ice and water. Many emf-temperature tables are, as a result, based on a 32° F. cold junction temperature.

It has been found that by using a small coil of alloy wire, the resistance of which has the desired change with temperature, it is possible for the cold junction to be at the ambient temperature of the case and yet have this coil automatically compensate for the difference between the case temperature and the base temperature of 32° F. Automatic cold junction compensators are incorporated in all of the potentiometer circuits of instruments installed on our process units as well as in many of our portable indicating potentiometers.

Types of Thermocouples

There are four different types of thermocouples being used in the refineries, namely, iron-constantan, copper-constantan, chromel-alumel and KA_2S-chromel. Practically all thermocouple measurements under 1100° F. which are made on process units use iron-constantan couples. KA_2S-chromel couples are used to measure the tube wall temperatures on the cracking furnaces and chromel-alumel couples are frequently used for flue gas and furnace temperatures.

The chromel-alumel couple is suitable for temperatures up to 2200° F. whereas iron-constantan does not retain its accuracy for long periods of time where temperatures are above 1000 or 1100° F. One advantage of the iron constantan in addition to being cheaper is that it is suitable for use in either oxidizing or reducing atmosphere whereas chromel-alumel can not be used in a reducing atmosphere unless every precaution is taken in designing the protecting tube to insure that it is impervious to gases.

Copper-constantan couples are frequently used in low temperature laboratory work as the copper is apparently more suitable for subzero temperatures than is the iron. This couple can be used in either oxidizing or reducing atmospheres but its top limit of temperature is about 600° F.

Liquid Level Measurement

Liquid level instruments, installed on towers and drums at points where it is desired to withdraw liquid products, are an essential part of an operating unit. Failure of one of these instruments permits the liquid to either rise and eventually flood the tower or fall to the point where vapor as well as liquid is being released through the liquid drawoff.

Liquid level can be measured by many different types of instruments but the ball float type is probably the simplest and, until recently, the one most frequently used on refinery installations. It consists of a hollow metal ball, 6 in. to 10 in. in diameter, attached to the end of a lever arm which in turn is connected to a horizontal shaft. This shaft extends from the inside of the vessel, where the float and lever arm are located, through a packing box to the outside of the vessel; thus, the shaft is free to rotate and can transmit any movement of the float to a pointer or pilot mechanism located on the outside of the vessel.

Frequently the ball float is mounted in a kidney shaped, pressure tight housing having a diameter only slightly larger than the float. This housing or float cage as it is termed is connected to the pressure vessel by 1½ in. or 2 in. piping at the point where it is desired to hold the level of the liquid in the vessel.

Objections to Ball Floats

Two objections to the ball float type of liquid level instrument are (1) the short range of float travel which is available and (2) the friction of the packing which tends to bind the shaft at the point where it passes through the packing box. A new type of instrument known as the displacement type has been developed within the past few years which does not have either of these two objections.

The float in this latter type of instrument is in the shape of a long, slim cylinder mounted with its axis in a vertical plane. The diameter of the float is about 3 in. and the length may vary, depending on the service for which it is purchased, from 14 in. to 120 in. Since this instrument is designed in such a manner that it can detect changes in liquid level over the entire length of the float, it is possible by using the 120 in. float to measure liquid level through a range of 10 ft.

Air-Operated Controllers

The discussion up to this point has covered the measuring systems used to determine temperatures, pressures, rates of flow and liquid levels. Any one of these four measuring systems can be combined with a pneumatic control system to form an air operated controller. A temperature controller, for example, used to hold the coil outlet of a furnace at a constant temperature would employ a thermocouple-potentiometer type of measuring system.

The pneumatic control system used in conjunction with the measuring system would include (1) an air pilot mechanism located in the same instrument case as the potentiometer, and (2) a pneumatically operated control valve installed in the line supplying fuel gas to the furnace burner. If the coil outlet temperature should begin to drop from the desired value or control point, the measuring circuit would detect this change and relay it to the air pilot which in turn would cause the control valve to release an additional amount of gas to the furnace.

The air pilot is supplied with compressed air from an external source and is connected by means of small diameter pipe or tubing to the diaphragm housing of the control valve. The purpose of the pilot is to serve as a relay between the measuring system and the control valve. Thus whenever the potentiometer detects a change in temperature, the pilot responds by either increasing or decreasing the air pressure in the piping leading to the control valve.

This air pressure acts on the control valve diaphragm which in turn is connected to the valve stem so that movement of the diaphragm either increases or decreases the port opening of the valve. Since the movement of the diaphragm is opposed on one side by a spring, any increase of the air pressure on the other side will force the diaphragm to move toward the spring. Thus the air pilot mechanism by changing the air pressure in the piping leading to the valve diaphragm housing can increase or decrease the quantity of fluid flowing through the body of the control valve.

Automatic Control

Temperature controllers similar to the type we have just described were supplied initially on the coil outlets of all furnaces which we have built during the past ten years. Furthermore, several furnaces which were originally controlled manually have in the last few years been equipped with automatic control.

Another application for this type of instrument is the control of the reboiler temperature on the bottom of a fractionating tower. The reboiler may be in the form of either a shell and tube type heat exchanger using steam or hot oil as the heating medium, or a direct fired heater.

The temperature controller in the case of the heat exchanger would hold a con-

Refinery engineer adjusts liquid level meter on a displacement or cylindrical float type of liquid level controller on butane tower reboiler

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stant temperature in the bottom of the tower by regulating the flow of the heating medium supplied to the exchanger. The control of a direct fired reboiler would be similar to that of the pipe still furnace described above.

The temperature at the top of a fractionating tower also is controlled automatically. The temperature sensitive element (thermocouple or other element) is installed in the vapor stream leaving the top of the tower and the control valve is located in the reflux line between the discharge of the reflux pump and the tower. The controller holds the top tower temperature constant by releasing more or less reflux to the tower depending on whether the temperature is tending to rise or fall from the control point.

Charges Stock Can Not Vary

It is almost impossible for a temperature controller on either a furnace or a tower to perform satisfactorily if the rate at which the charge stock is fed to the unit is permitted to vary. Therefore, a flow controller will be found on the feed to each unit.

A flow contoller is frequently used in conjunction with a temperature controller in regulating either the flow of fuel to a furnace or the flow of steam to a reboiler. Let us assume we are firing a furnace with fuel gas and one of the burner ports becomes partially plugged. The quantity of fuel being released into the furnace will as a result be decreased.

If we are using only a temperature controller to position the control valve in the fuel gas line there will be a considerable time delay before the temperature of the oil stream in the furnace coil begins to drop and this change is finally sensed by the thermocouple. The temperature controller will then respond to this temperature drop by opening the control valve an additional amount to compensate for the partial plugging of the burner but there will be another long time delay before the temperature of the coil outlet will return to the control point.

In contrast to this type of control action, a flow controller working in combination with the temperature controller would have responded immediately to the decrease in fuel gas flow and would have caused the control valve to open the required amount to compensate for the partial plugging of the burner port.

The orifice serving the flow controller would be installed in the fuel gas line and the diaphragm operated control valve also installed in the fuel gas line would be positioned directly by the air pilot mechanism of the flow controller. The air pilot mechanism of the temperature controller would be connected to a bellows located in the flow control instrument case and would function to raise or lower the control point of the latter instrument whenever the coil outlet temperature started to rise or fall.

ELEMENTS OF TERNARY DISTILLATION

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Most of the convenient graphical methods used in solving distillation problems involving binary mixtures cannot be applied to multicomponent mixtures, and somewhat cumbersome calculations must be resorted to. In dealing with ternary mixtures, however, the graphical methods of binary distillation can be used at least in part. This month the authors employ these graphical methods to solve several distillation problems involving ternary mixtures, thus presenting a clearer picture of multicomponent distillation than could be obtained from numerical calculations.

THE preceding papers of this series have presented the theory and computation of plate columns for the distillation of binary mixtures. The physical design of plate columns was also discussed. A knowledge of this material is a sufficient basis for understanding nearly all distillation phenomena in a qualitative way, since the graphical methods used showed the inter-relationship between energy and material balances and the equilibrium behavior of the system of components involved.

The distillation of mixtures containing a large number of components follows the fundamental principles which have already been presented. However, a large number of components eliminates in a large degree the possibility of using convenient graphical methods and the calculations, which now must be made numerically, are somewhat cumbersome and, because of this, sometimes confusing.

While the mixtures encountered commercially contain usually either two components or a relatively large number of components, a consideration of the distillation of ternary mixtures is helpful to an understanding of multicomponent distillation because it is possible to apply the graphical methods of binary distillation in part and thus obtain a relatively clear picture of the complications of multicomponent distillation not available from numerical calculations.

Vapor-Liquid Equilibria

The necessity of having an accurate knowledge of vapor-liquid equilibrium data in distillation calculations has been amply demonstrated in the preceding papers. For the purposes of this paper only ideal mixtures such as are often encountered in petroleum applications will be considered. Non-ideal vapor-liquid equilibria will be discussed in a later paper dealing with azeotropic and extractive distillation.

A mixture follows Raoult's and Dalton's law when the following equation may be used to describe the equilibrium behavior of each component.

$$Py_i = p_i x_i \quad \ldots\ldots (1)$$

where

P = total pressure, atm.,
p_i = vapor pressure of any component i at the temperature in question,
y_i, x_i = mole fraction of component i in the equilibrium, vapor and liquid respectively.

Rearranging Equation 1:

$$y_i = \frac{p_i}{P} x_i \quad \ldots\ldots (2)$$

In Equation 2, the quotient p_i/P is a function only of temperature and pressure and does not depend upon what other components are present or their concentrations. This is characteristic of an "ideal" solution.

Ideal solutions follow Raoult's and Dalton's laws only at low temperatures and pressures and it is customary to express the equilibrium behavior according to the equation

$$y_i = K_i x_i \quad \ldots\ldots (3)$$

where K_i = equilibrium volatility constant for component i

The relationship expressed by Equation 3 is followed by ideal solutions at all temperatures and pressures until the critical point of the mixture is approached. The equilibrium volatility constant, K_i, may be estimated by thermodynamic methods from pressure-volume-temperature data on the pure components or from experimental measurements, the most desirable source of data. Typical equilibrium constant curves are shown in Fig. 1, which presents the values of K for normal pentane, hexane, and heptane as a function of temperature and at 15 psia pressure.

Bubble Point Calculations—When a liquid mixture is at its bubble point, there is an infinitesimally small quantity of vapor in equilibrium with the liquid whose composition is known. Since the sum of the mole fractions of the vapor components must equal 1.0, Equation 4 may be used to calculate the bubble point temperature corresponding to a given pressure or the bubble point pressure corresponding to a given temperature.

$$\sum_{i=1}^{n} y_i = y_1 + y_2 + \ldots + y_n = 1.0 = \sum_{i=1}^{n} K_i x_i = K_1 x_1 + K_2 x_2 + \ldots + K_n x_n \quad \ldots\ldots (4)$$

Consider the following problem, No. 1: What is the bubble point temperature and the composition of the vapor in equilibrium with a liquid mixture containing 40 mole % normal pentane, 30 mole % normal hexane, and 30 mole % normal heptane at 15 psia pressure?

In solving this problem it is necessary first to assume a bubble point temperature. The K values for the components at the assumed temperature and the pressure are determined from Fig. 1. If the assumed temperature is correct, the sum of Kx's for the mixture must be equal to 1.0 according to Equation 4. If the assumed temperature is too high, the sum will be greater than 1.0, and if the assumed temperature is too low, the sum

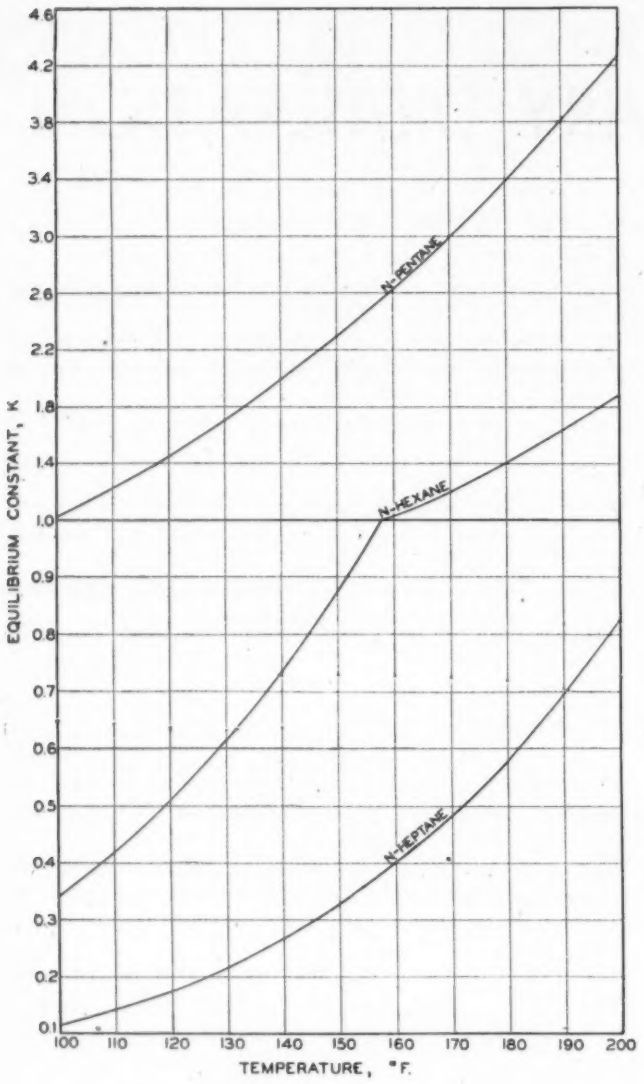

Fig. 1—Equilibrium volatility constants at 15 psia pressure

will be less than 1.0. By plotting the assumed temperatures versus the sums obtained, the correct temperature may be readily obtained. When the sum of the Kx's is equal to 1.0, the individual values of Kx are the mole fractions of the components in the vapor in equilibrium with the given liquid. The solution to the problem is shown in Table 1. When calculating the bubble point pressure at a given temperature, the bubble point pressure is assumed and the same procedure followed.

Dew Point Calculations—When a vapor mixture is at its dew point, there is an infinitesimally small quantity of liquid in equilibrium with the vapor whose composition is known. Since the sum of the mole fractions of the liquid components must equal 1.0, Equation 5 may be used to calculate the dew point temperature of a mixture at a given pressure or the dew point pressure at a given temperature.

$$\sum_{i=1}^{n} x_i = 1.0 = x_1 + x_2 + \ldots + x_n = \sum_{i=1}^{n} \frac{y_i}{K_i} = \frac{y_1}{K_1} + \frac{y_2}{K_2} \ldots + \frac{y_n}{K_n} \quad \ldots\ldots (5)$$

Consider the following problem, No. 2: What is the dew point temperature and composition of liquid in equilibrium with a vapor of the composition of Problem No. 1 at 15 psia pressure?

In solving Problem No. 2, a dew point temperature is assumed, the K values at the assumed temperature and 15 psia are evaluated from Fig. 1, and the sum of y/K terms evaluated. If the assumed temperature is too high, the sum will be less than 1.0 and if too low, the sum will be greater than 1.0. The mole fraction of a given component in the liquid in equilibrium with the given vapor is the value of the individual y/K for that component when the sum of the y/K's is equal to 1.0. The solution is shown in Table 2.

Vaporization Calculations—When a mixture is partially vaporized, the relation between the equilibrium concentrations of the various components given by Equation 3 must be combined with a material balance in order to compute the quantity of vaporization and the compositions of the equilibrium liquid and vapor.

By an overall material balance

$$F = L + V \quad \ldots\ldots (6)$$

where

F = moles of feed mixture partially vaporized,
L = moles of equilibrium liquid,
V = moles of equilibrium vapor.

By a component balance

$$Fz_i = Lx_i + Vy_i \quad \ldots\ldots (7)$$

where z_i = mole fraction of component i in the feed.

Since $y_i = K_i x_i$, substituting in Equation 7

$$Fz_i = x_i(L + VK) = y_i\left(\frac{L}{K} + V\right) \quad \ldots\ldots (8)$$

Rearranging

$$x_i = \frac{F}{V}\left[\frac{z_i}{L/V + K_i}\right] \text{ and } y_i = \frac{F}{V}\left[\frac{K_i z_i}{L/V + K_i}\right] \quad \ldots (9)$$

Also

$$\sum x_i = 1.0 = \frac{F}{V}\sum \frac{z_i}{L/V + K_i} \quad \ldots\ldots (10a)$$

and

$$\sum y_i = 1.0 = \frac{F}{V}\sum \frac{K_i z_i}{L/V + K_i} \quad \ldots\ldots (10b)$$

Consider the following problem, No. 3: What is the per cent vaporization of the mixture of Problems 1 and 2 when brought

TABLE 1—Solution of Problem No. 1

Component	Liquid Composition, mole fraction	Assumed Temperature 130° F. K	130° F. Kx	135° F. K	135° F. Kx	134.5° F. K	134.5° F. Kx	Correct Kx
n-C_5	0.4	1.708	0.6840	1.842	0.7370	1.825	0.7300	0.7287
n-C_6	0.3	0.615	0.1844	0.674	0.2022	0.667	0.2002	0.1999
n-C_7	0.3	0.217	0.0651	0.241	0.0723	0.238	0.0715	0.0714
	1.0		0.9335		1.0115		1.0017	1.0000

TABLE 2—Solution of Problem No. 2

Component	Vapor Composition mole fraction	Assumed Temperature 180° F. K	180° F. y/K	170° F. K	170° F. y/K	Corrected y/K
n-C_5	0.4	3.390	0.1180	2.995	0.1337	0.1331
n-C_6	0.3	1.408	0.2132	1.200	0.2500	0.2489
n-C_7	0.3	0.580	0.5172	0.483	0.6208	0.6190
	1.0		0.8487		1.0045	1.0000

TABLE 3—Solution of Problem No. 3

Component			Assume L/V=1.5, V=0.4		Assume L/V=1.222, V=0.45		Assume L/V=1.247, V=0.445		Liquid composition mole fraction	Material Balance	Vapor composition mole fraction
	z	K 150°	K+1.5	$z/(K+1.5$	K+1.222	$z/(K+1.222)$	K+1.247	$z/(K+1.247)$	F/V $\Sigma z/(K+1.247)$	$z-[z/(K+1.247)]$	
n-C_5	0.4	2.290	3.790	0.1056	3.512	0.1140	3.537	0.1132	.254	0.2868	0.517
n-C_6	0.3	.875	2.375	0.1263	2.097	0.1431	2.122	0.1414	.318	0.1586	0.286
n-C_7	0.3	.329	1.829	0.1640	1.551	0.1935	1.576	0.1904	.428	0.1096	0.197
				0.3959		0.4506		0.4450	1.000	0.5550	1.000

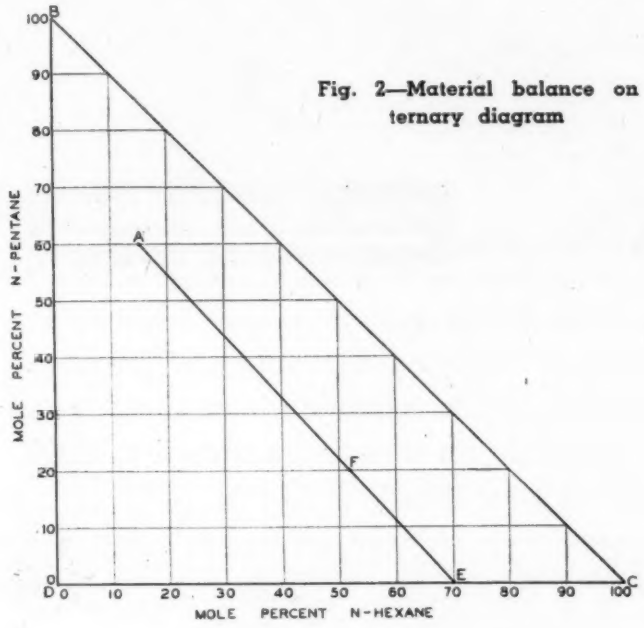

Fig. 2—Material balance on ternary diagram

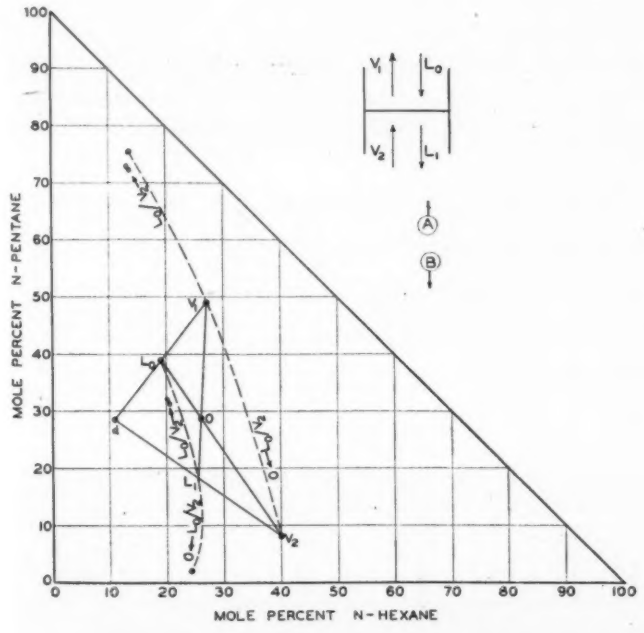

Fig. 3—(A)—Diagrammatic equilibrium plate. (B)—Composition diagram for a single equilibrium plate

to a temperature of 150° F. and 15 psia. pressure? Also what are the vapor and liquid compositions under these conditions?

In solving this problem the per cent vaporization is assumed, L/V calculated and the summations of the right hand side of either Equation 10a or Equation 10b is calculated. This summation is equal to 1.0 when the correct assumption of per cent vaporization has been made. The compositions of the vapor can be obtained by a material balance once the per cent vaporization has been obtained and the liquid composition determined. Table 3 shows the solution to Problem No. 3, using Equation 10a.

Enthalpy Data for Multicomponent Mixtures

In general, experimental data from which the enthalpy composition relationships of multicomponent mixtures can be evaluated are exceedingly meagre. However, since hydrocarbon mixtures are more or less ideal, it is permissible in most cases, to assume that the enthalpy relations are such as to give constant molal overflow conditions in fractionating columns over a wide range of temperature, pressure and composition. With high pressure columns, the assumption of ideal solutions and a knowledge of the thermodynamic properties of the pure hydrocarbons permits a correction of the assumption of constant molal overflow by means of repeated enthalpy balances for various sections of the columns. However, in this discussion constant molal overflow will be assumed since the examples to be discussed involve ideal mixtures and low temperatures and pressures.

Graphical Material Balances for Ternary Mixtures

The composition of a ternary mixture containing components such as pentane, hexane and heptane may be conveniently represented by plotting the mole fraction of one of the components as a function of the mole fraction of another component, as shown in Fig. 2. Since the sum of the three mole fractions must equal one, it is necessary to specify only the mole fractions of two of the components in order to completely define the composition of the mixture. Thus, the point *A* of Fig. 2 represents a mixture containing 60 mole % pentane, 15 mole % hexane and 25 mole % heptane. The complete range of possible compositions are represented within the right triangle *BCD*, the point *B* representing 100 mole % pentane, point *C* representing 100 mole % hexane and point *D* representing 100 mole % heptane.

The plot of Fig. 2 is similar to the enthalpy-composition plots for binary mixtures shown in previous articles, since a composition variable has been substituted for the enthalpy variable. A plot such as Fig. 2 may be used in making material balances for ternary mixtures in the same way that the enthalpy-composition plots were used in making enthalpy and material balances for binary mixtures. Thus, if 100 parts of a mixture containing 60 mole % pentane, 15 mole % hexane and 25 mole % heptane represented by point *A* are added to 200 parts of a mixture containing 10 mole % hexane and 30 mole % heptane represented by point *E*, the resulting mixture will be represented by the point *F* lying on the straight line *AE* so that the ratio of distances

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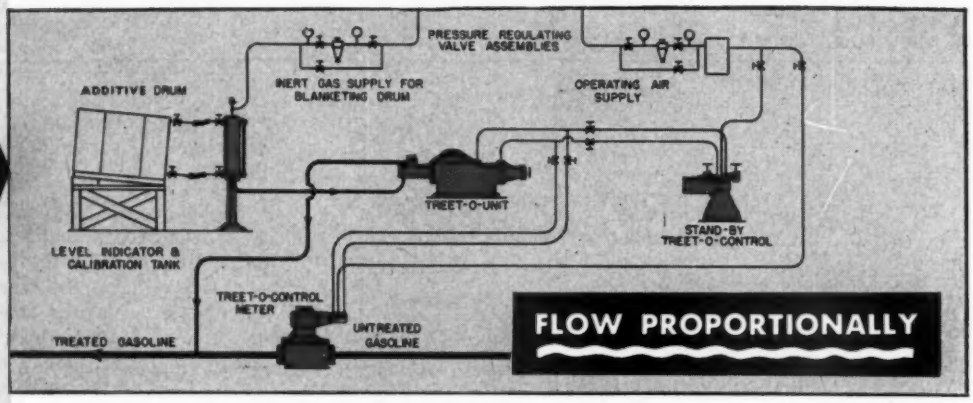

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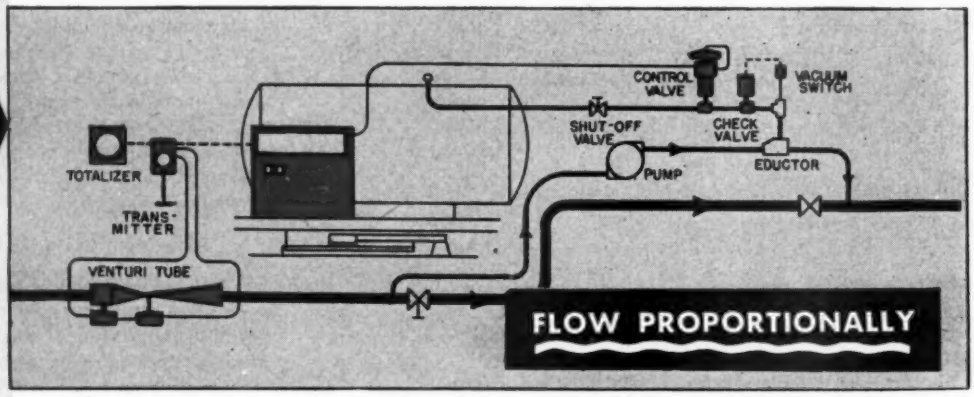

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TABLE 4—Summary of Calculations for Single Equilibrium Stage

Single stage at 15 pounds per square inch absolute pressure with saturated feeds where $L_0/V_2=2.0$

FEED STREAMS

Component	L_0, moles	L_0, mole fraction	V_2, moles or mole fraction	L_0+V_2, moles
n-C_5	0.78	0.39	0.08	0.86
n-C_6	0.38	0.19	0.40	0.78
n-C_7	0.84	0.42	0.52	1.36
	2.00	1.00	1.00	3.00

FIRST TRIAL

Component	Assumed L_1 moles	L_1, mole fraction	K162° F	Kx	Correct Kx $=V_1$ moles	L_1+V_1
n-C_5	0.40	0.20	2.698	0.539	0.542	0.942
n-C_6	0.38	0.19	1.058	0.201	0.202	0.582
n-C_7	1.22	0.61	.417	0.254	0.256	1.476
	2.00	1.00		0.994	1.000	3.000

FINAL TRIAL

Component	Assumed L_1 moles	L_1, mole fraction	K162.5° F.	Kx	Corrected Kx $=V_1$, moles	L_1+V_1 moles
n-C_5	0.364	0.182	2.715	0.494	0.493	0.857
n-C_6	0.508	0.254	1.067	0.271	0.270	0.778
n-C_7	1.128	0.564	.421	0.237	0.237	1.365
	2.000	1.000		1.002	1.000	3.000

AF/FE = 200/100. The previous philosophy regarding difference points[1] also applies.

Equilibrium Stage Calculations

The operation of a single equilibrium stage is shown in Fig. 3a, corresponding to one idealized plate of a plate fractionating column. A saturated liquid L_0 and a saturated vapor V_2 are fed continuously to this stage where they are mixed. The mixed phases separate into the vapor V_1 and the liquid L_1 which leave the stage and which by definition are in equilibrium.

The saturated liquid and vapor feed streams are represented by the points L_0 and V_2, respectively, on the composition diagram, Fig. 3b. The point O, representing the sum of the liquid and vapor feeds, is located on the straight line, L_0V_2, so that the ratio of the distances OV_2/OL_0 equals the ratio of the quantities of the feed streams, L_0/V_2. The sum of the liquid and vapor feeds to the stage must equal the sum of the equilibrium liquid and vapor leaving the stage, and, therefore, the vapor, V_1, and the liquid, L_1, are represented by the terminal points of the equilibrium tie line which passes through the point O.

Furthermore, it is assumed for the purposes of this calculation that the conditions of constant molal overflow, previously described[2], are met by this system and, therefore, the quantity of liquid, L_1, leaving the stage will equal the quantity of liquid fed to the stage, L_0, since L_0 is a saturated liquid at its boiling point.

Similarly, the quantity of vapor, V_1, leaving the stage will equal the quantity of vapor, V_2, fed to the stage, since V_2 is a saturated vapor at its dew point. Thus, the ratio L_1/V_1 equals L_0/V_2 and the relative distance OV_1/OL_1 will be equal to the relative distance OV_2/OL_0.

In consequence, if the composition and quantities of the saturated feed streams are given, it is necessary to locate the equilibrium line L_1V_2, passing through the point O and divided into segments by the point O according to the ratios $L_1V_1 = OV_1/OL_1$. This is a trial and error calculation which is summarized in Table 4 for the case L/V = 2.0, and the composition of the saturated feed streams as shown in the table. The results of these calculations are shown in Fig. 3b.

The composition of a liquid L_1 must be assumed and the composition of the vapor V_1 in equilibrium with the assumed liquid calculated by means of Equation 4. As can be seen from the diagram, the composition of the vapors has been enriched with respect to normal pentane, the most volatile component, has not been changed appreciably with respect to the normal hexane, the component of intermediate volatility, and has been depleted with respect to normal heptane, the less volatile component. Similarly, the liquid has been enriched with respect to the least volatile component, normal heptane, and depleted with respect to the most volatile component, normal pentane. The calculations for the composition diagram are summarized in Table 4.

The difference between the liquid L_0 and the vapor V_1 passing one another above the stage is equal to the difference between the liquid L_1 and the vapor V_2 passing one another below the stage. This difference is represented by the point d, which is located by the intersection of the lines L_1V_2 and L_0V_1. The quantity ratios L_1/V_2 and L_0/V_1 are equal to the distance ratios dV_2/dL_1 and dV_1/dL_0, respectively.

The effect of changing the ratio of the feed streams to the stage and the composition of the streams leaving the stage may be followed by repeating the above calculations. It is clear that when the ratio L_0/V_2 approaches infinity the point O representing the sum of the two feed streams will approach the point L_0. Thus, the composition of the vapor V_1 will approach the condition of equilibrium with L_0 and the composition of the liquid L_1 will become equal to the composition of the liquid L_0. Similarly, as the ratio L_0/V_2 approaches O, the point O will approach the point V_2, the composition of the vapor V_1 will become identical with the composition of the vapor V_2 and the composition of the liquid L_1 will approach a condition of equilibrium with the vapor V_2. The paths which are followed by the liquid L_1 and the vapor V_1 as the ratio L_0/V_2 is varied from O to infinity is shown by the dotted lines in Fig. 3b.

Where the feed streams, L_0 and L_2, are not saturated, it is necessary to incorporate a heat balance into the calculation in order to determine the new ratio L_1/V_1. The difficulties inherent in rigorous multicomponent fractionation calculations are illustrated by this problem, which resolves itself into what might be considered a "double trial and error" calculation.

Consider the following problem in which the feed streams

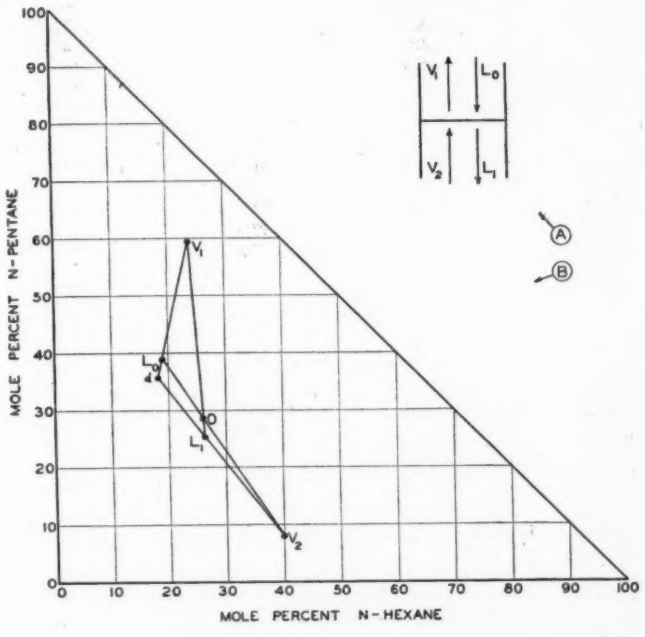

Fig. 4—(A)—Diagrammatic equilibrium plate. (B)—Composition diagram for a single equilibrium plate with unsaturated feeds

supplied to an equilibrium stage are the same as in the previous problem except that the liquid feed, L_0, is at 80° F. and the vapor feed, V_2, is at 195° F. The ratio of the feed streams, L_0/V_2, = 2.

The solution to this problem is shown in Table 5 and on Figs. 4a and 4b. In the calculations it is necessary to assume a composition and quantity of either the liquid, L_1, or the vapor, V_1, leaving the stage. From this assumption the other product leaving the stage can be determined from equilibrium calculations. This is done until the material balance is satisfied. When the material balance checks, it is necessary to make an enthalpy balance around the stage. The solution to the problem is obtained when both the material balance and the enthalpy balance are satisfied simultaneously. The enthalpy data used in the calculations was presented by Holcomb and Brown[3].

Several Equilibrium Stages

The operation of a system of three equilibrium stages to which saturated feeds, mixtures of normal pentane, normal hexane, and normal heptane are fed is shown in Figs. 5a and 5b, where $L_0/V_4 = 2$. The point L_0 represents the saturated liquid fed to the top stage and the point V_4 represents the saturated vapor fed under the bottom stage of the column. The sum of the feed streams L_0 and V_4 is represented by the point O located on the straight line L_0V_4, such that the ratio of the distances OV_4/OL_0 equals the ratio of the feed quantities L_0/V_4.

Again, the sum of the feed streams equals the sum of the

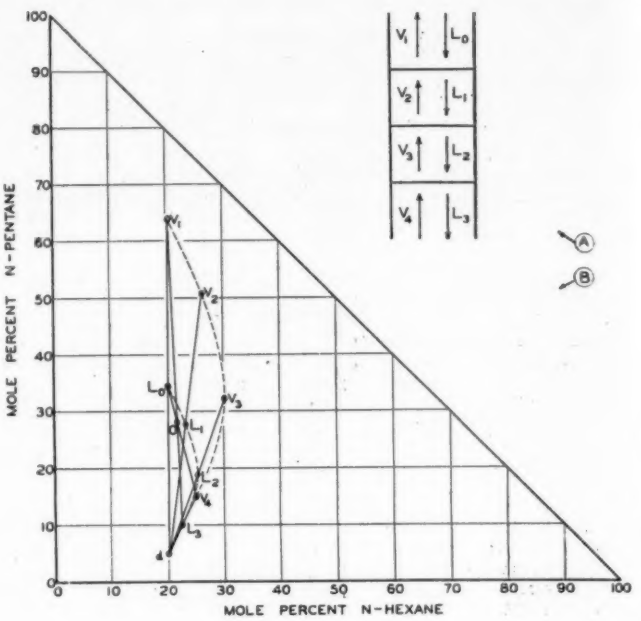

Fig. 5—(A)—Diagrammatic three plate column. (B)—Composition diagram for three stage column

TABLE 5—Summary of Calculation of Single Equilibrium Stage with Unsaturated Feed

FEED STREAMS, ENTHALPY AND MATERIAL BALANCE

Component	L_0, moles	Enthalpy, h at 80° F. Btu/# mole	Enthalpy of L_0 Btu's	V_2, moles	Enthalpy, H at 195° F. Btu/# mole	Enthalpy of V_2 Btu	Enthalpy $L_0 + V_2$ Btu	$L_0 + V_2$ moles
n-C_5	0.78	1850	1440	0.08	13800	1105	4320	0.86
n-C_6	0.38	2120	805	0.40	14870	5945	15270	0.78
n-C_7	0.84	2470	2075	0.52	15860	8220	.....	1.36
	2.00		4320	1.00		15270	19590	3.00

ASSUME L_1 = 2.5 MOLES, FINAL TRIAL ON MATERIAL BALANCE

Component	Assumed L_1, mole fraction	K154° F.	Kx	Corrected $Kx = V_1$, mole fraction	L_1, moles = 2.5L_1, mole fraction	V_1, moles = 0.5 × V_1, mole fraction	$L_1 + V_1$, moles
n-C_5	0.235	2.418	0.568	0.574	0.587	0.2870	0.874
n-C_6	0.260	0.931	0.242	0.245	0.650	0.1225	0.7725
n-C_7	0.505	0.355	0.179	0.181	1.263	0.0905	1.3535
	1.000		0.989		2.500	0.5000	3.0000

ENTHALPY BALANCE FOR FINAL COMPOSITIONS FOR L_1 = 2.5

Component	L_1, moles	Enthalpy, h at 154° F. Btu/# mole	Enthalpy of L_1, Btu's	V_1, moles	Enthalpy, H at 154° F. Btu/# mole	Enthalpy of V_1, Btu	Enthalpy of $V_1 + L_1$
n-C_5	0.587	4990	2930	0.287	12560	3630	14860
n-C_6	0.650	5730	3720	0.1225	13390	1640	6550
n-C_7	1.263	6500	8210	0.0905	14130	1280	.....
			14860	0.5000		6550	21410

ASSUME L_1 = 2.7 MOLES, FINAL TRIAL ON MATERIAL BALANCE

Component	Assumed L_1, mole fraction	K152° F.	Kx	Corrected $Kx = V_1$, mole fraction	L_1, moles = 2.7L_1, mole fraction	V_1, moles = 0.3 × V_1, mole fraction	$V_1 + K_1$, moles
n-C_5	0.253	2.357	0.596	0.5965	0.683	0.179	0.862
n-C_6	0.263	.902	0.2372	0.2374	0.710	0.071	0.781
n-C_7	0.484	.343	0.1660	0.1661	1.307	0.051	1.357
			0.9992	1.0000	2.700		3.000

ENTHALPY BALANCE FOR FINAL COMPOSITION FOR L_1 = 2.7 (FINAL RESULT)

Component	L_1, moles	Enthalpy, h at 152° F. Btu/# mole	Enthalpy of L_1, Btu's	V_1, moles	Enthalpy, H at 152° F. Btu/# mole	Enthalpy of V_1 Btu's	Enthalpy of $V_1 + L_1$
n-C_5	0.683	4880	3330	0.179	12480	2235	15650
n-C_6	0.710	5610	3990	0.071	13300	945	3895
n C_7	1.307	6380	8330	0.051	14030	715	.....
	2.700		15650	0.300		3895	19545

product streams, L_3 and V_1, and the point O must be on the line L_3V_1, such that the ratio of the distances OV_1/OL_3 equals the ratio of the quantities L_3/V_1. Also, since constant molal overflow is assumed, the ratio L_3/V_1 must be equal to the ratio L_0/V_4, since the quantities of liquid, L_0 and L_3, are equal and the quantities of vapor, V_4 and V_1, are equal.

The difference between the liquid feed, L_0, and the vapor product, V_1, which pass one another above the top plate, equals the difference between the vapor feed, V_4, and the liquid product, L_3, which pass one another below the bottom plate of the column. The point d which represents this difference, is located at the intersection of the lines L_0V_1 and L_3V_4.

The difference between the liquid and vapor passing one another above the top plate and below the bottom plate is also equal to the difference between the liquid and vapor passing one another between any two plates of the column; that is, between V_2 and L_1, and V_3 and L_2. Therefore, point d is the common point of intersection of the straight lines drawn through all pairs of points representing the liquid and vapor passing one another between any two stages of the column.

The vapor, V_3, leaving the bottom plate of the column is in equilibrium with the liquid, L_3, leaving the bottom plate and thus the point V_3 is located on an equilibrium tie line from the point L_3. The point L_2, representing the liquid leaving the second plate of the column, is located on the line dV_3 such that the ratio of the distances dV_3/dL_2 is equal to the ratio of the quantities L_3/V_4. Having located the point L_2, the vapor V_2, leaving the second plate of the column is located at the end of the equilibrium tie line from L_2. The point L_1, representing the liquid leaving the top plate of the column, is located on the line dV_2 such that the ratio of the distances dV_2/dL_1 is equal to the ratio of the quantities L_1/V_2, which in turn is equal to the ratio of the quantities L_0/V_4, since constant molal overflow is assumed.

The above calculation involves a trial and error procedure, since it is necessary to assume either the liquid, L_3, or the vapor, V_1, leaving the column in order to begin the calculations. The bottom product, L_3, is assumed and the overhead product is located by drawing a line through the point O from L_3 terminating at the point V_1, so that the ratio of the distances OV_1/OL_3 is equal to the ratio L_0/V_4. The plate construction is carried out as described above for the three plates, and if the correct L_4 was assumed the composition of the vapor leaving the top plate will coincide with the point V_1, determined from the overall material balance. The calculations for the composition diagram, Fig. 5b, are summarized in Table 6 where $L_0/V_4 = 2.0$ and pressure of operation is 15 psia.

TABLE 6—Summary of Calculation for Three Equilibrium Stages

FEED STREAMS

Component	L_0, moles	L_0, mole fraction	V_4, moles	$L_0 + V_4$, moles
n-C_5	0.688	0.344	0.150	0.838
n-C_6	0.402	0.201	0.250	0.652
n-C_7	0.910	0.455	0.600	1.510
	2.000		1.000	3.000

PLATE 3—FINAL TRIAL

Component	Assumed L_3, moles	L_3, mole fraction	K177° F.	$Kx = V_3$	$L_3 - V_4$, moles	$V_3 + L_3 - V_4 = L_3$, moles
n-C_5	0.200	0.100	3.268	0.3268	0.05	0.3768
n-C_6	0.450	0.225	1.343	0.3020	0.20	0.5020
n-C_7	1.350	0.675	0.550	0.3712	0.75	1.1212
	2.000	1.000		1.0000	1.00	2.0000

PLATE 2—FINAL TRIAL

Component	L_2, mole fraction	K-161° F.	Kx	Corrected $Kx = V_2$, moles	$V_2 + L_2 - V_4 = L_1$, moles
n-C_5	0.1884	2.660	0.5050	0.507	0.557
n-C_6	0.2510	1.043	0.2620	0.263	0.463
n-C_7	0.5606	0.409	0.2290	0.230	0.980
	1.0000		0.9960	1.000	2.000

PLATE 1—FINAL TRIAL

Component	L_1, mole fraction	K149.5° F.	Kx	Corrected $Kx = V_1$, moles	$L_3 + V_1$, moles
n-C_5	0.2785	2.273	0.634	0.638	0.838
n-C_6	0.2315	0.866	0.201	0.202	0.652
n-C_7	0.4900	0.325	0.159	0.160	1.510
	1.0000		0.994	1.000	3.000

As the ratio L_0/V_4 approaches infinity, the composition of the vapor product V_1 approaches a condition of equilibrium with L_0 as in the case of a single stage, since the point O representing the sum of the feed streams approaches the point L_0. Also, the composition of the liquid product L_3 approaches the composition of the liquid feed L_0. Similarly, as the ratio L_0/V_4 approaches O, the composition of the liquid leaving the bottom plate approaches a condition of equilibrium with the vapor V_4 and the composition of the overhead vapor approaches the composition of the feed vapor. Again, the paths followed by the liquid and vapor product as the ratio L_0/V_4 is varied are shown by the dotted lines in Fig. 6 for the three plate column.

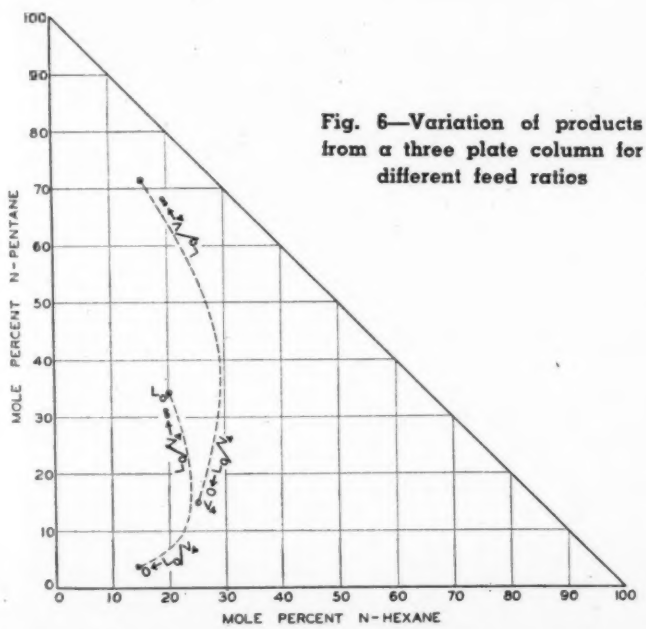

Fig. 6—Variation of products from a three plate column for different feed ratios

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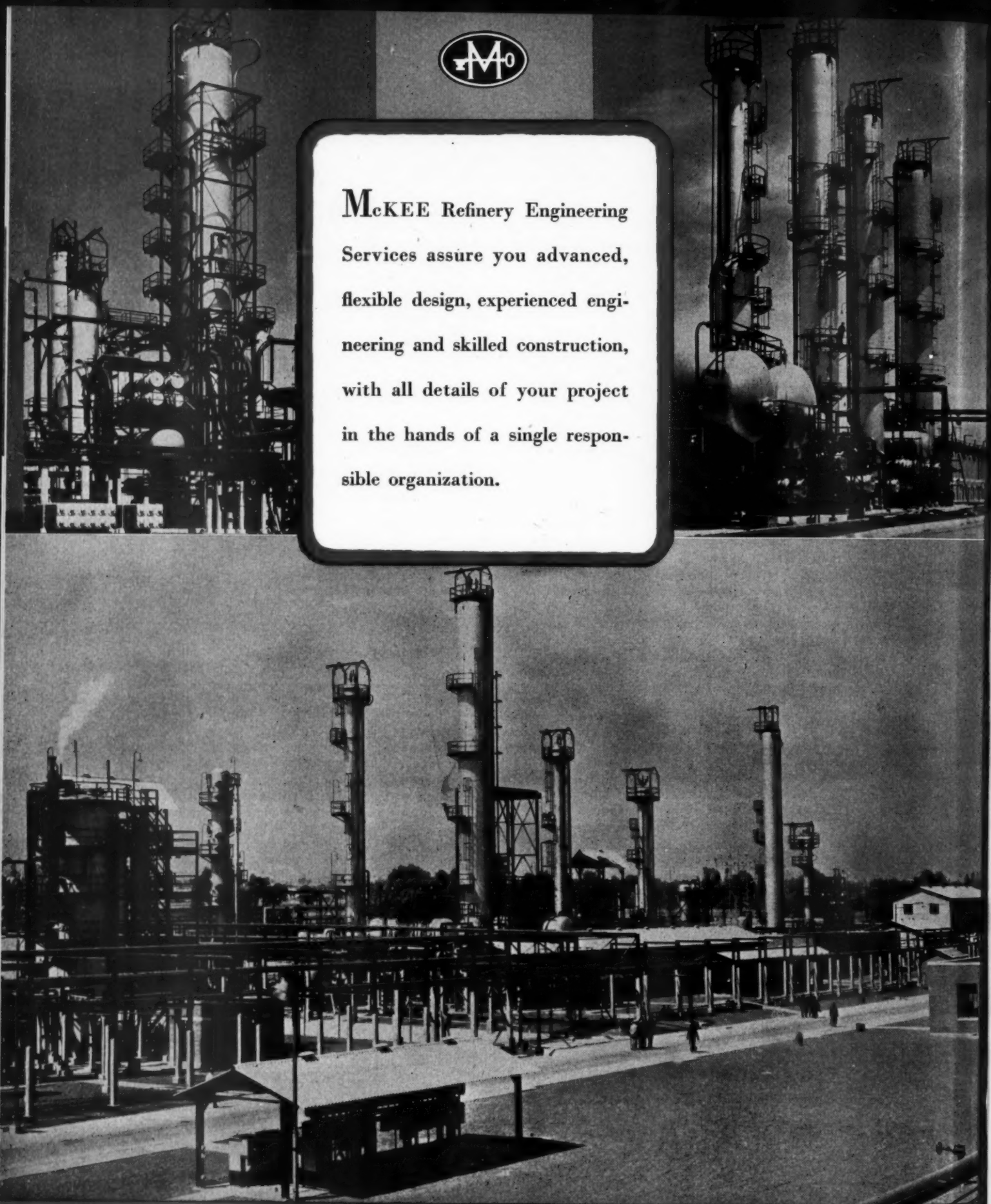

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UNDIVIDED RESPONSIBILITY IN ONE ORGANIZATION

Patent Trends in Petroleum Refining

By Peter J. Gaylor

Patent Attorney and Editor "The Technical Survey"

Developments disclosed in the patents reviewed below include:

A newly-developed process for the continuous production of greases.

HF acid-resistant packing made of a mixture of talc and flake graphite.

Use of the hydrate of boron fluoride for treating hydrocarbon oils.

Removal of aromatics by selective adsorption with silica gel.

Low-pour point synthetic lubricants using dicarboxylic acid esters.

Continuous Process for Manufacture of Greases

LAST year there was disclosed (NPN *Technical Section*, Aug. 7, 1946, pg. R-586) a continuous process for producing greases, patented by the Standard Oil Development Co. Lately, another method has been patented by the Girdler Corp. (U. S. 2,417,495) wherein use is made of annular heaters, coolers and workers to facilitate the processing of the materials.

Fig. 1 illustrates a flow sheet of one modification of the process wherein an oil-soap mixture from mixing kettle 10 is deaerated in vacuum chamber 21 and pumped through a heating unit 18, details of which are shown in Fig. 2. This is a jacketed cylinder with heating fluid coming in through line 32 and leaving through 33, while the soap slurry enters at 34 around rotating cylinder 28 and leaves through line 35 after being scraped off the cylinder by scrapers 29.

The grease is then again submitted to deaeration in vacuum chamber 43, and thereafter it is cooled in cooler 38, similar in construction to the heater shown in Fig. 2. The cooled mass is finally worked in working unit 57, shown in Fig. 3. In the case of some greases, such as those of the lithium type, it is desirable to allow a little aging time, by passing the grease through vessel 98 before working in unit 57.

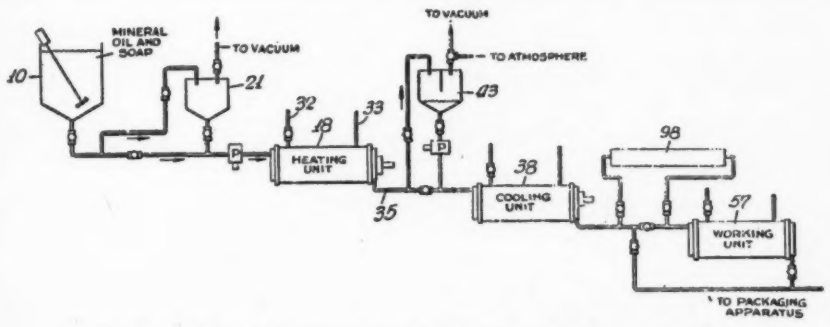


Fig. 1—Flow diagram for the Girdler Corp.'s continuous process for manufacturing greases (U. S. 2,417,495)

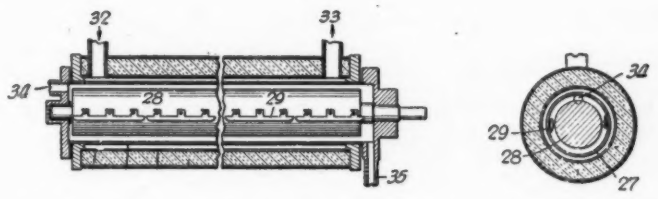


Fig. 2—Side and end views of the heating unit for Girdler's continuous grease manufacturing process

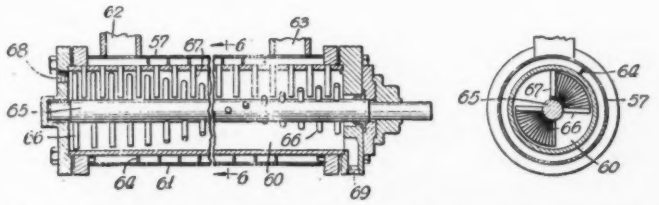


Fig. 3—Side and end views of the working unit for Girdler's continuous grease manufacturing process

Pump Packing Made of Talc Resists Hydrofluoric Acid

HYDROFLUORIC alkylation plants are sometimes troubled with leaks in circulating pumps and control valves, mainly due to the corrosive action of the acid upon the packing material. Such leaks constitute a serious health hazard due to the high toxicity of the acid.

One of the patents issued to Socony-Vacuum Oil Co. (U. S. 2,417,351) discloses the use of a packing and lubricating mass consisting of an intimate mixture of talc and flake graphite, the talc being present in an amount of 75-90% of the total weight of the mixture. It is said to be surprising that talc is so effective, since it is essentially a siliceous material ($MgO \cdot 4SiO_2 \cdot H_2O$), and therefore would be expected to be attacked by hydrofluoric acid. The graphite is added to afford a lubricating quality to the talc.

Treating and Desulfurizing Oils With Boron Fluoride Hydrate

THE use of one mole of boron fluoride with one mole of water ($BF_3 \cdot H_2O$) is employed in a Phillips Petroleum Co. patent (U. S. 2,416,465) for removing sulfur compounds and unsaturated hydrocarbons from hydrocarbon oils such as alkylate, hydrocodimer, straight run gasoline, kerosine, cracked gasoline and coal tar aromatics.

It has been found that, whereas dry boron fluoride is without chemical action on pure thiophene, for example, the hydrate of boron fluoride vigorously attacks

the compound with the evolution of hydrogen sulfide. Organic sulfides and mercaptans react with the hydrate to form polar complex compounds insoluble in hydrocarbons but miscible with excess hydrate.

The treating method consists of merely agitating the hydrocarbon distillate with boron fluoride hydrate, settling, and separating the hydrate with its dissolved sulfur and polymer. The distillate is then washed with dilute alkali to remove traces of hydrate and hydrogen sulfide.

In one example, catalytically cracked naphtha of 10 bromine number and containing 0.301 wt.-% sulfur (and having a rich mixture rating of S + 0.2) was treated with the hydrate at 75° F. The treated naphtha had an S + 5.2 rating, a bromine number of 1, and a sulfur content of only 0.004%.

An extreme case of removal of olefinic material was illustrated by the treatment of 300 E.P. debutanized gas-plant gasoline with boron fluoride hydrate. The bromine number of the unfractionated untreated stock was about 50. Continuous treatment was carried out at 125° F. until 25 volumes of hydrocarbon charge had been treated per volume of $BF_2 \cdot H_2O$. The treated stock was washed and the following data were obtained on the fractions:

Fractions	Bromine Number Before	After
80°-110° F.	60	0.4
110°-300° F.	45	3.0
Kettle product	..	40.0

It is apparent that the reagent effectively polymerizes the unsaturates to higher boiling products.

Separation of Aromatics

WORK done during the past few years has shown that much of the carbon deposition on cracking catalyst is due to the presence of small amounts of polynuclear aromatics. Mononuclear hydrocarbons such as benzene, toluene, etc. do not possess this characteristic to such an extent. Hence, the selective separation of polynuclear aromatics is considered important in such cases.

Universal Oil Products Co. has described the use of silica gel for effecting such a separation (as shown in its U. S. patent 2,395,491). Table 1 shows the selectivity of this adsorbent for removing polynuclear aromatics, as illustrated by alpha methyl naphthalene, from mononuclear hydrocarbons, such as triethyl benzene. The original mixture, diluted to five times its original volume with pentane, and containing 46 wt.-% of triethyl benzene and 54% of methyl naphthalene, was passed through a fixed bed of 12-20 mesh silica gel having a bed depth of 14 in. A total of 82 cc. of the solution were passed downwardly over the adsorbent, giving the results shown in Table 1. It will be observed that the first cuts are quite rich in the mononuclear triethyl benzene.

TABLE 1—Separation of Aromatics with Silica Gel (U. S. 2,395,491)

Cut No.	Grams of Aromatics	Wt.—% on Aromatics Charge	n_D^{20}	Composition, wt.—% Triethyl-benzene	-Methyl naphthalene
1	0.21	1.4	1.4809	....	....
2	2.55	16.4	1.5143	84	16
3	3.59	23.2	1.5410	57.5	42.5
4	7.18	46.4	1.5787	23	77
TOTAL	13.53	87.4	.....	....	....

TABLE 2—Lubricant Properties of Dicarboxylic Acid Esters (U. S. 2,417,281)

Name of ester	Centistokes viscosity at— 210° F.	100° F.	—40° F.	Slope on ASTM viscosity-temp. chart for the interval of 210° F. to —40° F.	Visc. index	Flash point	Pour point, ° F.	Approx. boiling point, ° F. at atmospheric pressure
Di sec. butyl sebacate	2.09	6.42	320	0.752	136	355	—90	650
Di-2-ethylhexyl sebacate	3.31	12.64	1,532	0.707	152	430	—90	760
Di-undecanyl sebacate	4.66	22.83	8,000	0.716	138.5	...	—85	...
Di-2-ethylhexyl alkylated succinate	5.56	42.72	200,000*	0.812	68.5	...	—45	...
Di-2-ethylhexyl azalate	3.05	11.25	1,200	0.729	147	410	—40	750

* Extrapolated from the 100 and 210° F. values.

Instrument Lubricants Employ Dicarboxylic Acid Esters

PETROLEUM oils are generally useful and desirable for most lubricating and hydraulic purposes. But they have their limitations. For example, pour points of below —30° F. and particularly below —60° F. are practically impossible to obtain with petroleum lubricants, since the freezing points of the oil hydrocarbons themselves are generally above these figures. Also, petroleum lubricants have a tendency to creep over metal surfaces. Although this property is an advantage in many lubricating applications, it is an unwanted property in other applications, such as in instrument and watch lubrication.

A recent patent to Standard Oil Development Co. (U. S. 2,417,281) discloses the formulation of instrument lubricants by the use of certain dicarboxylic acid esters, particularly di-2-ethylhexyl sebacate. Table 2 lists the properties of a number of esters in this class, most of which possess low pour points and very high viscosity indices.

It has been found that the lower the initial neutralization number of the sebacate ester, the higher is its stability against oxidation, as measured by the Staeger test. The following composition was found to have excellent properties, including low creeping tendency (as measured by the multiple pin spreading test):

Di-2-ethylhexyl sebacate	99.4%
2,6-Ditertiary butyl P-cresol	0.5
Alkyl succinic acid	0.1

The addition of 0.05% of zinc naphthenate was found to also inhibit rusting of steel, as measured by the ASTM turbine oil rust test. The claims of the patent specify the use of calcium petroleum sulfonates as the soap ingredients.

Weed Killer

An item under the heading "Asphaltic Weed Killer" in the March issue of PETROLEUM PROCESSING ("Patent Trends in Petroleum Refining," p. 186) made reference to Sovasol No. 75, a Socony-Vacuum Oil Co. product, as a selective weed killer for application to fields of carrots, parsnips and parsley.

Our attention has been called to the fact that the material which is employed as a selective herbicide for carrots is Sovasol No. 5, rather than Sovasol No. 75. "Sovasol No. 75," the company states, "if applied directly to carrots would injure them, whereas Sovasol No. 5 kills only the weeds and not the growing crop."

Selected Patents of the Month

U.S. 2,417,826 (Continental Oil Co.)—Lubricant containing metal sulfide fused with phosphorus sulfide and sulfur.

U. S. 2,417,827 (Continental Oil Co.)—Lubricant containing inorganic tetrathiophosphate.

U.S. 2,417,833 (Continental Oil) — Lubricant containing silicon compound.

U. S. 2,417,872 (Standard Oil Development Co.)—Dimethyl butene from propylene.

U. S. 2,417,875 (Phillips Petroleum Co.)—Removing HF from water.

U.S. 2,417,876 (Tide Water Assoc. Oil Co.)—Lubricant inhibited with thiophosphoric-sulfonic acid compounds.

U.S. 2,417,877 (Stand. Oil Dev. Co.)—Automatic oxygen indicator.

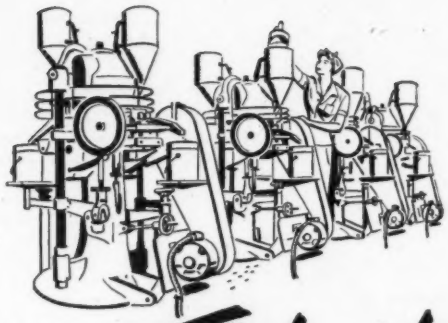
U.S. 2,417,892-3 (Sinclair Refining Co.) — Amines and nitriles.

U.S. 2,417,955 (Phillips Petr. Co.)—Lockable pipe connection.

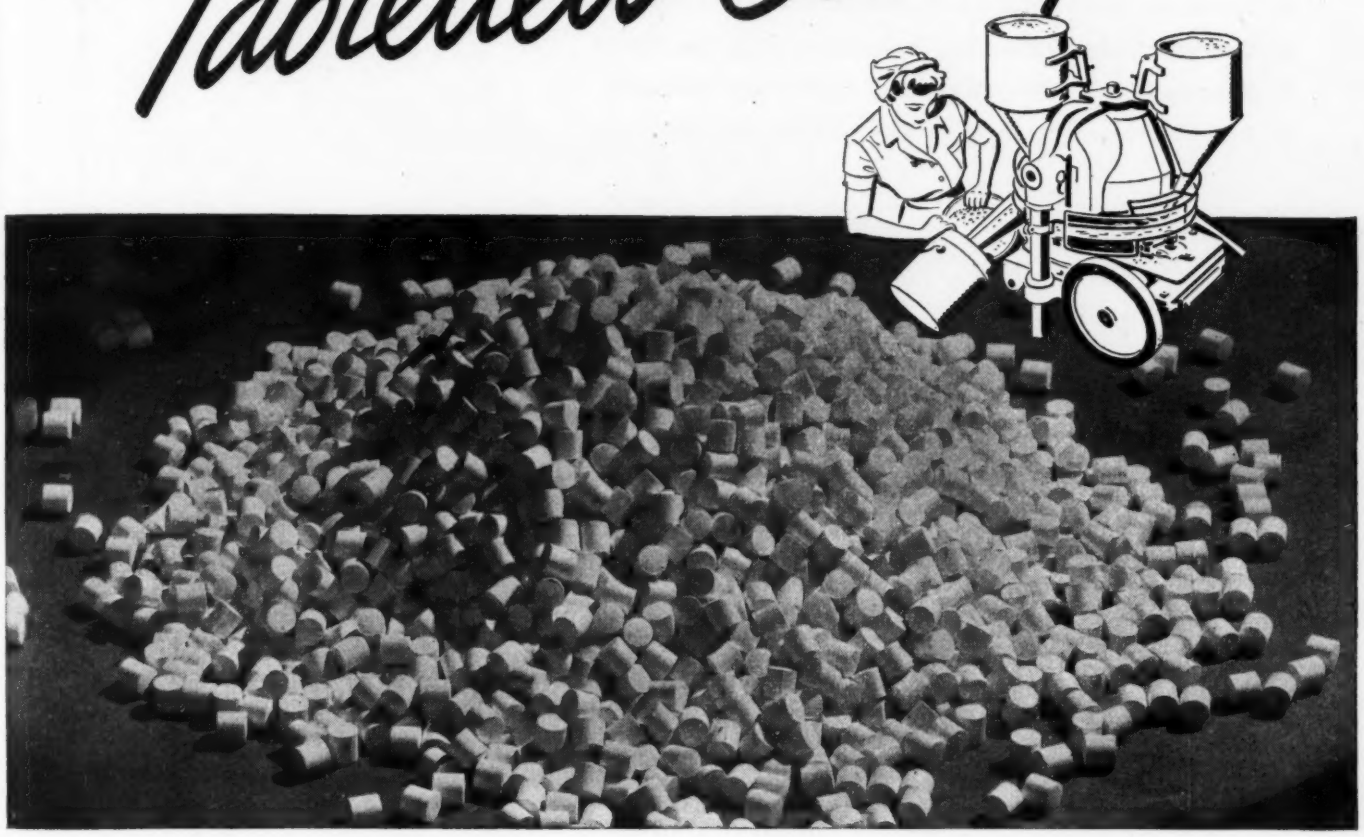
U.S. 2,418,023 (Phillips Petr. Co.)—Isobutane from low boiling olefine.

U.S. 2,418,075 (Union Oil Co.)—Rust preventive.

U.S. 2,418,173 (Shell Dev. Corp.)—Diketones.



Tabletted Catalysts



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High Recovery, Low Steam Use In Improved Absorption Unit

In addition to the improved absorption unit for oil purification described below, this month's review of new and improved devices used in petroleum processing and handling operations on which patents have recently been issued include:

- **Sectional liners reduce wall cracks in catalyst chambers**
- **Carriage reduces damage in removing pipe line filters**
- **Automatic fire extinguisher uses carbon tetrachloride**
- **Added downcomer increases bubble column efficiency**

MATERIAL SAVINGS in steam consumption and an improved recovery are said to be possible with a continuous absorption oil purifier comprising a still, a secondary purifier, and a dephlegmator.

Essentially a steam distillation process, the apparatus is shown in the simplified flow diagram in Fig. 1. Fat oil enters the system via pipe 31; the major portion of it—about 99% or more—goes directly into the main stripper still 29. The balance passes through line 34 to the secondary still 30, flow being controlled by regulator 32 and valve 33.

Stripped oil passes from still 29 to vessel 30 via line 44 and 51. The major portion of the overhead—stripped gasoline hydrocarbon vapors and steam—passes via line 35 into the midsection of still 30, where it flows upward and distills a portion of the rich absorption oil. The higher boiling ends not distilled are subjected to the action of live steam entering through line 47.

Overhead from purifier 30 passes on through line 38 to dephlegmator 39, where the adjusted heat balance condenses the absorption oil vapors. The finished separated products pass out as indicated in the drawing.

The still, strippers, and dephlegmator can be typical bubble cap columns or may be filled with other conventional types of contact packing.

In one example of actual operation, the steam rate to the stripper 29 was 10,000 lbs./hr. for stripping 30,000 cu. ft. of hydrocarbon vapors from the rich oil. The combined stream then passed into purifier 30 into which 150 gals./hr. of rich oil flowed—about 0.5% of the feed. 97% of the feed to the stripper 30 was distilled. The undistilled portion, constituting high boiling ends and the usable portion of this material was distilled by the use of only 3000 lbs./hr. of steam.

By this last operation, 80% of the absorption oil previously lost was saved as overhead distillate, making an overall recovery of 97 + 0.80 × 3, or 99.4%.

U. S. 2,417,007, issued March 4, 1947, to Charles O. Meyers, assignor to Phillips Petroleum Co.

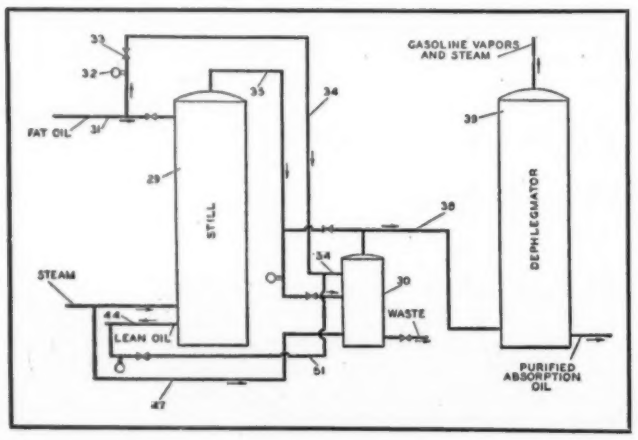


Fig. 1 — Apparatus for effecting high recovery of absorption oil with low steam consumption (U. S. 2,417,007)

Sectional Liners Reduce Wall Cracks in Catalyst Chambers

CASTING heat-insulating liners in catalyst chambers in a plurality of sections and providing a grooved joint between each section is said to reduce the formation of objectionable cracks extending along the length of the chamber shell.

As shown in Fig. 2, a conventional catalyst chamber 10 has an outer asbestos covering 17 and the inner lining 18, made of some cast insulating material, preferably of the refractory type.

The liner consists of sections 19, 20, 21, and 22, each provided with a V-shaped

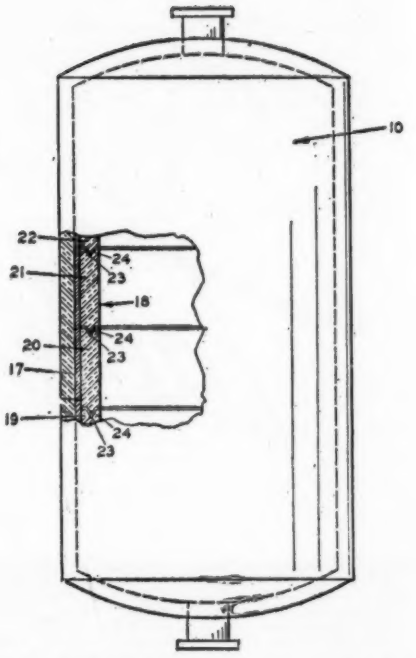


Fig. 2—Partial cross section, showing construction of liners for catalyst chamber (U. S. 2,417,348)

groove 23 and corresponding tongue 24. In the course of construction the lowest section is cast into the shell and allowed to set or substantially solidify. Groove 23 is then formed. As soon as it has set, it is coated with a suitable sealing material and the entire operation is repeated until the inside wall has been lined.

If desired, additional tongues and grooves may be formed at each joint. Their purpose is to hinder the passage of any fluid by virtue of the extended path so formed.

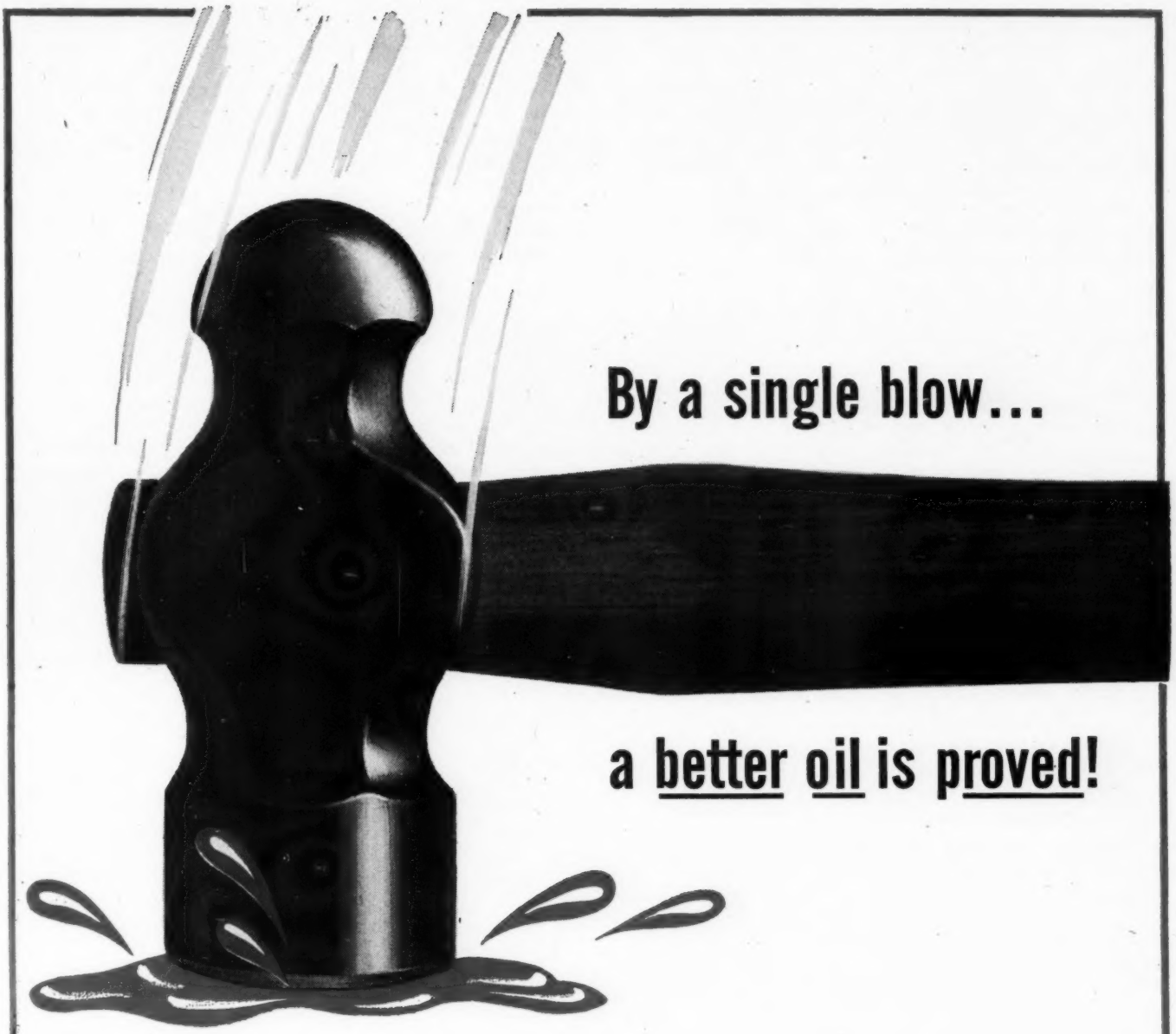
U. S. 2,417,348, issued March 4, 1947, to Charles E. Carter, assignor to Phillips Petroleum Co.

Carriage Reduces Damage in Pipe Line Filter Removal

REMOVAL of the filtering element without damage by means of a simple carriage arrangement is provided in a recently patented filter for use on pipe lines for light hydrocarbons such as butane, gasoline, kerosene, and the like.

The unit is shown in a closed position in Fig. 3, and in an open position, supported by the carriage, in Fig. 4. Fluid to be filtered enters at pipe 11, passes through the felt blanket 23, the expanded metal lathe 22, perforations 21, filter cylinder element 20, and out through pipe 34. Sludge accumulations are removed occasionally via pipe 36; however, periodic removal and cleaning or complete replacement, of the filter element is necessary.

The carriage 44 fits around pipe 34 and into holes in the outer flange by means of lugs 46, as shown in detail in Fig. 5, and in Fig. 4. Carriage wheels



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PARATONE —*for improved viscosity index.*
PARAFLOW —*for lower stable pour.*
PARATAC —*for tacky oils and greases.*
PARAPOID —*for E.P. gear oils.*
PARANOX —*for inhibiting corrosion and oxidation.*
PARASHEEN —*for better appearance.*
PARADYNE —*for improved gasoline.*

ENJAY COMPANY, INC.

*Trade Marks

26 BROADWAY, NEW YORK 4, NEW YORK • AGENTS AND DISTRIBUTORS THROUGHOUT THE WORLD

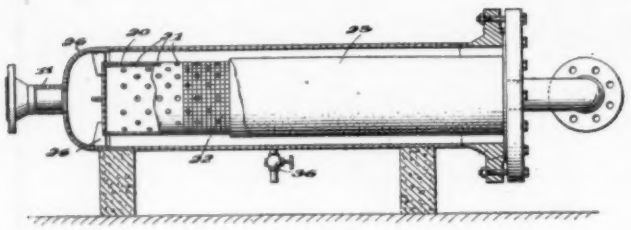


Fig. 3—Longitudinal section view of improved pipe line filter (U. S. 2,417,000) which provides for maintenance and cleaning without damage to unit

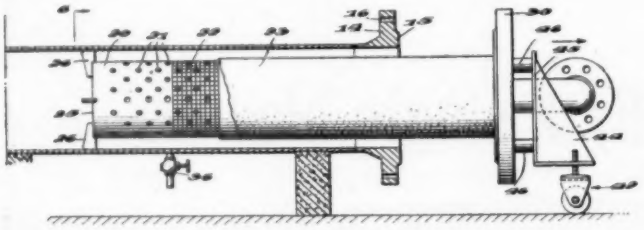


Fig. 4—Pipe line filter unit with filter element partially removed and mounted on special carriage

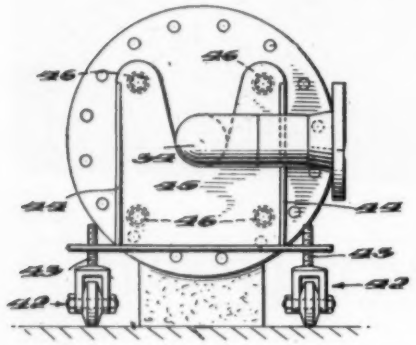


Fig. 5—End view detail of carriage construction

42 can be adjusted for height variations by means of threaded fittings 43.

When the filter element is pulled out from the casing, fins 26, spaced around the circumference of the element, maintain its horizontal position.

Because filter elements are usually heavy and cumbersome, this arrangement is said to prevent damage to not only the felt blanket and the metal lathe, but also to the element itself.

U. S. 2,417,000, issued March 4, 1947, to Edgar A. Koenig, assignor to Socony-Vacuum Oil Co. Inc.

Automatic Fire Extinguisher Uses Carbon Tetrachloride

An Ordinary Container of carbon tetrachloride can be converted to an automatic fire extinguisher by attaching a specially designed adaptor to the opening.

The device consists of a perforated shell for spraying the extinguishing fluid and a fusible metal mechanism which releases a spring-loaded plunger so as to break the frangible disc seal.

Two forms of the device are shown in Fig. 6. The standard container is indicated at 30 with a male threaded opening at 29. The frangible disc 32 is placed between two washers and the adaptor is screwed into place. Plunger 25 is held against spring 31 in socket 23 by means of the fusible metal pin 26 through shaft 24.

In operation, heat from a fire melts pin 26, releasing plunger 25 and breaking the disc. The container itself is suspended in an inverted position above the hazardous location.

A modified form of the same adaptor device, also for use on standard metal containers of carbon tetrachloride, uses a typical mousetrap spring arrangement for breaking the frangible disc. In this one, the plunger is again held in the cocked position by means of a fusible metal pin. However, the pin is on the top of the adaptor instead of the bottom as shown in the drawing.

U. S. 2,417,374, issued March 11, 1947, to C. R. Morton, Summit, N. J.

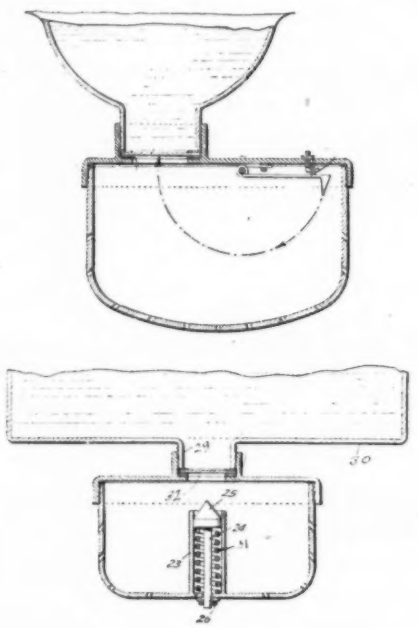


Fig. 6—Two types of adaptors for converting standard container of carbon tetrachloride to automatic fire extinguisher (U. S. 2,417,374)

Added Downcomer Increases Bubble Column Efficiency

Use Of Two downcomer pipes on each plate provides a bubble cap column which will handle and control both nonadhesive solids and two or more liquid phases, it is claimed.

It is said to be particularly applicable to separation of polymerizable monomers, where solid and semi-solid materials formed cause occasional shutdowns for cleanout. In addition, certain absorption processes; for example, furfural, involve a water phase as well as a polymer phase, which precludes efficient, intimate, countercurrent contact between vapor and the lighter of the two liquid phases.

A cross-section of a tower with two of the new type plates and additional downtakes is shown in Fig. 7. Bubble caps 16 and downcomers 42 are conventional. Light phase liquid is indicated at 57, heavy phase at 55, and solid particles at 54.

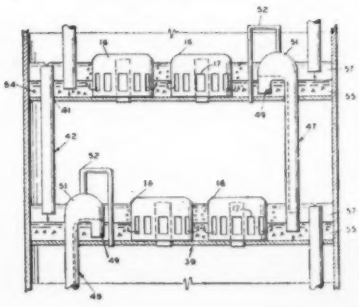
Light phase liquid 57 flows downward in conventional manner through pipes 42. Heavy phase 55 is transferred through J-tubes 47 and 48, being forced up short leg 49 and over bend 51 when a sufficient quantity has accumulated in the tray.

Conduit 52, leading from the vapor space to bend 51, prevents a siphoning action which would draw too much liquid off the tray. The velocity of the flow through downcomers 47 and 48 tends to carry solid particles along with the heavy phase liquid.

Other advantages of the device are said to be as follows: A solid or immiscible liquid catalyst, inhibitor, or the like, may be used in the column, being fed at the top. Foaming does not interfere with the operation. Vapor entrainment with downflowing liquid, a serious limitation on the capacity of some downtakes, is eliminated or greatly reduced. Use of the two downcomers at opposite ends of the tray produces a countercurrent flow of the two liquid phases across the plate.

U. S. 2,416,724, issued March 4, 1947, to Thomas H. Whaley, assignor to Phillips Petroleum Co.

Fig. 7—Added downcomers 47 and 48 enable bubble plate to handle two liquid phases as well as solid particles (U. S. 2,416,724). Conduit 52 prevents siphoning action



What's New!

EQUIPMENT . . . MATERIALS . . . PROCESSES . . . LITERATURE

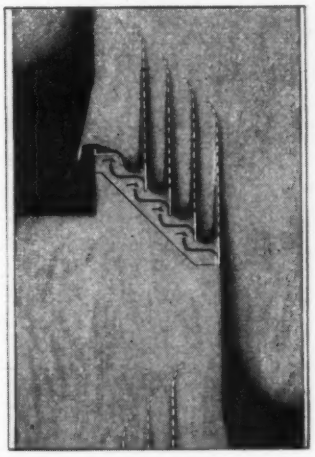
1—Small Air Compressor

"Unitair" is a complete new line of two-stage, air-cooled, stationary air compressors. They are available in nine sizes with power requirements ranging from 15 to 100 hp, and piston displacements from 81 to 590 cfm at 100 psi discharge pressure, based on 60 cycle motor speeds. Three standard drives include built-in motor, direct-connected motor, and V-belt drive. Features include: force-feed lubrication by gear-driven pump—"Cascade" oil cooling to reduce oil consumption and sludging—low-lift, large port-area, direct concentric valves—low piston speeds—oversize ball-type main bearings—four piston rings per piston mounted above the pin. Sullivan Division, Joy Manufacturing Co.

2—Fractionating Tray

The Kaskade fractionating tray is said to have a capacity about 150% that of the conventional bubble tray. A vertical section of the new design is shown in the drawing. Trays are available for tower sizes from 2½ to 10 ft.

In operation, liquid entering through a downcomer from the tray above is fed into one of the parallel vapor streams rising from the tray below, and the resulting mixture is hurled against a solid plate to which is attached a perforated baffle. The velocity of the mixture creates considerable centrifugal force as the mixture flows along the baffle, forcing all of the liquid and much of the vapor through the perforations. The liquid separates from the vapor on the other side of the baffle to feed into the next trough, where the operation is repeated. Due to the stair-step arrangement of troughs, large quantities of liquid can be handled with no build-up from one trough to the next. Koch Engineering Co., Inc.



3—Welding Electrode

"Nicast" is a new welding electrode said to put cast iron in a class with steel for ease of welding and finishing. It is made to operate on either AC or DC power. Welds produced by the electrode are strong and non-porous, and can be drilled, tapped, milled, or machined. Most applications will require no preheating or post-heating, and welds will withstand hydrostatic pressure. Available in either ⅛ or 5/32 x 14 in. sizes. The Harnischfeger Corp., Welding Division.

4—Multipoint Alarm Cabinet

All remotely located analysing heads in this new combustible gas alarm system are controlled from a single cabinet occupying a floor area only 22 in. wide by 17¼ in. deep. The system provides for sampling from a minimum of 6 to a maximum of 12 points. The installation consists of an analysing head in each area being sampled, and the central control cabinet.

A sampling pump in the cabinet continuously draws gas samples through all heads. A timer connects each analyser head consecutively with an indicating meter. Each connection is maintained for 10 seconds, although the timer can be made to stop and hold any particular head for further observation. Davis Emergency Equipment Co., Inc.

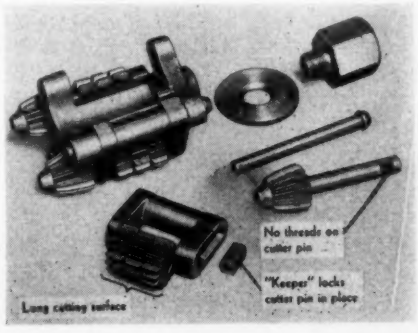
5—Boiler Feedwater Treatment

Liquon Silica-Removal Process applies the principles of demineralizing to the removal of silica from raw boiler feed water. The process employs a standard demineralizing plant, consisting of a Liquon hydrogen zeolite unit followed by a Liquon anion exchange unit. To effect the elimination of silica, a fluoride such as sodium fluoride is added to the raw water feed to zeolite unit. Here, the fluoride is converted to hydrofluoric acid by a resin type of acid-regenerated cation exchange material known as Liquonex CR. The acid combines with the silica to form fluorsilicic acid while, at the same time, the Liquonex CR converts the raw water hardness into the acids corresponding to the salts present. In the anion exchange unit, the fluorsilicic acid and the acids formed from the hardness in the water are removed by Liquonex A, an alkali-regenerated anion exchange resin of high capacity. Liquid Conditioning Corp.

6—Heavy Duty Tube Cleaner

An improved swing-frame type of tube cleaner cutter head has been developed for use in straight tubes in refinery and other heavy-duty service. It is said to overcome one disadvantage of this type cutter head by replacing usual threaded cutter pin with a "keeper," which fits into a slot in the arm and locks into a groove in the cutter pin.

The head is available in seven sizes, accommodating 2¼ to 6 in. I. D. tubes. Lagonda Division of Elliott Co.

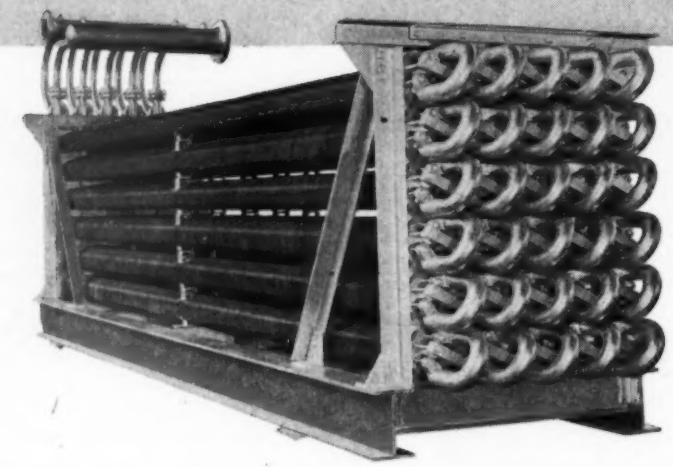


For More Information

Use one of the attached business reply cards, which requires no postage, to request additional details or literature on any items reviewed in "What's New!" Just circle the numbers corresponding to the numbers on the items you're interested in, fill in the bottom of the card, and drop it in the mail.

Slow to foul—easy to clean

G-R TUBEFLO SECTION



Dirty or sediment-carrying fluids are constant sources of trouble and service expense when heated or cooled in conventional designs of heat transfer apparatus.
However, here is a heat exchanger that has proven its superiorities for more than fifteen years and in 4000 installed units, handling cracking coil residuum, crude oil, fluxed asphalt, clay-bearing oil, and on similar duties.

- ONE TUBE PER PASS . . .
- CONTINUOUS HIGH VELOCITY . . .
- NO POCKETS . . .
- NO INTERLEAKAGE BETWEEN FLUIDS . . .

In the G-R Tubeflo Section, all passages, including return bends, are of uniform area, so that continuous high velocity of the fluids carries tar or sediment completely through the unit. In many instances these units are maintaining initial capacity indefinitely on services which had previously necessitated shut-down and cleaning of shell-and-tube units before the end of a single run. When shut-downs for cleaning are necessary, the large-diameter tubes minimize cleaning time and effort.
But greater freedom from clogging and greater ease of cleaning are only two of the many advantages of the G-R Tubeflo Section. For complete information on these units, write for our Bulletin 1621.

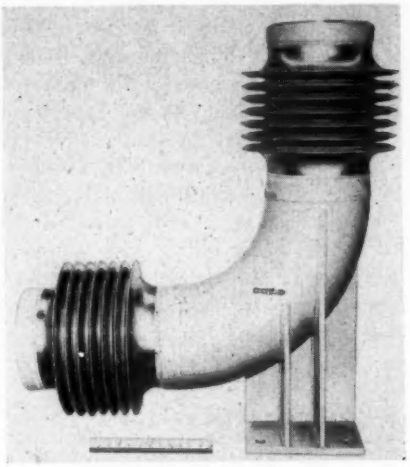
THE GRISCOM-RUSSELL CO.
285 Madison Avenue, New York 17, N. Y.

GRISCOM-RUSSELL
Pioneers in Heat Transfer Apparatus

What's New!

7—Elbow Expansion Joint

A new packless anchor base elbow expansion joint can be supplied in all standard pipe sizes and in a choice of materials to meet special corrosive, temperature, and pressure conditions. The illustration shows a 10 in. pipe size unit approximately 4 ft. high, built to accommodate 40 psi steam pressure. Each bellows allows 1½ in. total movement with 30 in. overall free length. The bellows are fabricatetd from stainless steel, and the ell is standard weight 10 in. carbon steel pipe. The joint shown was designed for operation up to 360° F. Magnilastic Division, Cook Electric Co.



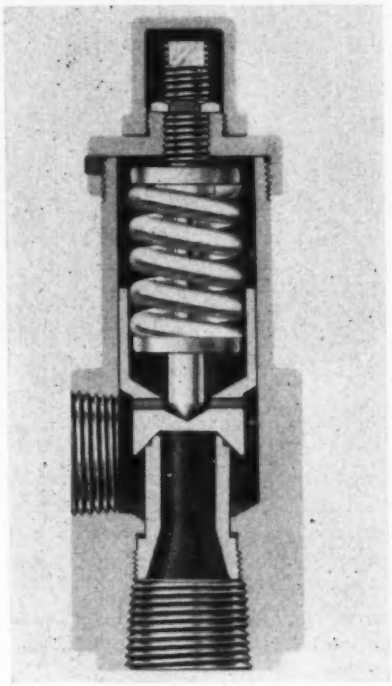
8—Welding Electrode

For welding low alloy cast steel or low alloy tensile strength rolled steels in all positions, with alternating-current or direct-current reverse polarity, the new ACP-MO electrode is available in four diameters from 3/32 to 3/16 in. Although designed primarily for AC use, it is said to be exceptionally good for DC, reverse polarity. Welds made with this electrode meet the requirements of AWS-ASTM tentative specifications for Iron and Steel Arc Welding Electrodes, Classification E-7011. Westinghouse Electric Corp.

9—Static Electricity Indicator

The Statometer is a portable, self-contained instrument for the detection and measurement of electrostatic voltage conditions. Weighing 5 lbs. 10 ozs., and measuring 10¾ in. high by 4¾ deep by 6 wide, it is calibrated in terms of static volts. It is said to be sensitive enough to detect static charges on the order of fractional volts. Provided with a 2- position scale range switch, it is possible to measure any voltage from 0 to 750. The position of the meter needle indicates positive or negative charges. Davis Emergency Equipment Co., Inc.

10—High Pressure Relief Valve

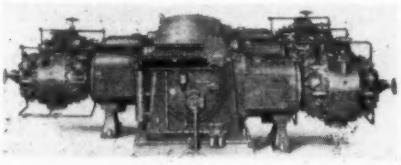


A relief valve for pressures up to 10,000 psi, fabricated completely from bar stock, either bronze, cold rolled steel, or stainless steel. In all cases, the disc and nozzle are of stainless steel. Available with or without test gear, in three body sizes—½, ¾, and 1 in. Interchangeable nozzle inserts provide for proper capacity at set pressures in three ranges —2,000, 5,000 and 10,000 psi for each size. Inlet and outlet connections are tapped directly into the valve body. Loading spring is completely enclosed. Nozzle seat is well above the drain line, remaining dry, and is not subject to accumulations of scale and sediment. Farris Engineering Corp.

11—Air Compressor

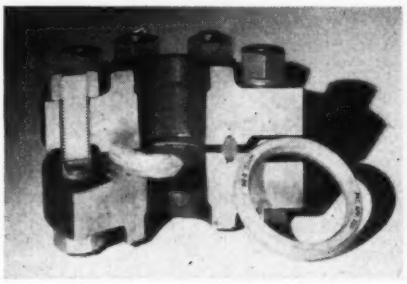
The "JM" series of air compressors are said to offer considerable space saving possibilities. Six sizes are available, ranging in dimensions from 11 ft. 7 in. to 24 ft. 6 in. in length, and from 13 ft. 9 in. to 24 ft. 2½ in. in width. Horsepower range is 500 to 2750. Compressor stroke is 14 in., operating at 300 rpm. Power can be taken from a standard synchronous electric motor, an engine or a turbine. All cast parts are Meehanite.

Compressor cylinders are interchangeable with Type GMV. Provision can be made for low vacuums or high pressures, as well as for all intermediate conditions. Cylinder valves are standard ring-plate type and are self cleaning. Valve seats are renewable, and interchangeable from suction to discharge. Automatic control of flow or pressure is available through electrical or mechanical unloading by means of suction valve lifters. Cooper-Bessemer Corp.



12—Insulating Gasket

A Fiberglas-plastic ring seal gasket has been designed to meet oil and gas well corrosion problems, and is available in all standard sizes. It is a high-strength, high-dielectric, laminate consisting of plies of glass cloth impregnated with a phenolic resin, and precision molded under high pressure and temperature. It provides insulation against stray and long line electric currents and also eliminates galvanic corrosion at the joint. It has a flat compression strength of 66,245 psi, an edge compression strength of 15,757 psi, and a tensile strength of 48,272 psi. Temperature limit is 480° F. Plastic Engineering and Sales Corp.

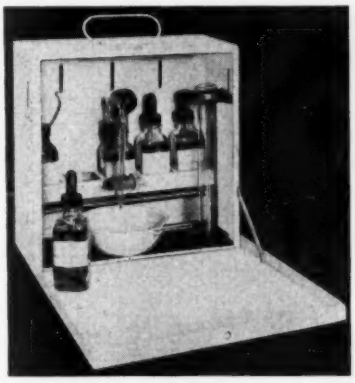


13—Air Velocity Meter

A new ultra-sensitive air velocity meter will measure accurately to as low as a 5 ft./min. rate. The principle of operation, based on a combination of the hot-wire and thermopile principles, increases the accuracy of the instrument by minimizing the errors due to air temperature variations.

The pickup element is a noble-metal thermopile placed in the air stream. Alternate junctions are arranged to have much greater cooling than the adjacent junctions, which are heated by passing alternating current through the wire. The instrument operates on 110 volts AC, and may be adapted for remote indication. The output is suitable for operating standard strip or circular chart recording instruments. The standard range is from 0 to 2000 ft./min.; 50 ft./min. is approximately 20% of full scale. Hastings Instrument Co., Inc.

14—Water Analyses Kit



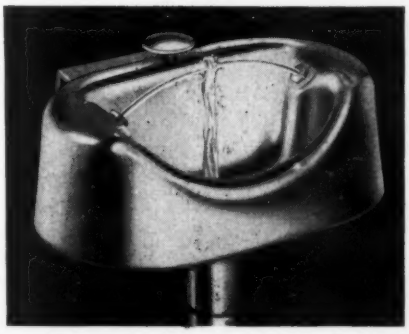
A compact, portable kit for on-the-job analyses of water conditions, the Trutest unit is contained in a heavy gage steel cabinet and measures 9¾ x 9¾ x 4¾ in. The unit can be carried about or hung at any required location by the slotted holes in the back wall.

Working chemicals in the kit include phenolphthalein indicator, 5% sulfuric acid, potassium chromate, and N/25 silver nitrate for titrations. Other equipment is a 50 ml. graduate, stirring rod and dish, and an automatic micro-burette. Results are read directly from the burette in grains of chloride per gallon, using a 100 ml. sample of the water to be tested. Trutest Laboratories, Inc.

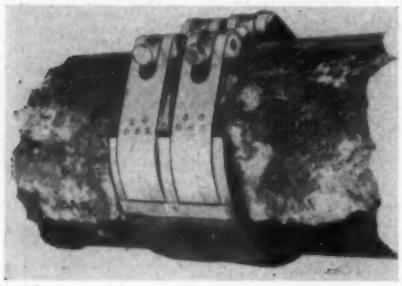
15—Eye Wash Fountain

A new emergency eye-wash fountain is operated by placing the head in a cast aluminum bowl, designed to fit the upper contours of the face. In this way, it is necessary to keep the eyes in the ideal range of the two streams of water. In addition, it allows freedom of the hands to spread the eyelids apart, assuring contact of the water with every portion of the eye tissues which have been contacted by foreign substances.

A pressure regulator built into the actuating valve produces a soft stream assuring copious but easy flow. The device is essentially a double fountain with standard inlet and drainage connections. Invented by Benson & Associates, Inc.; manufactured by Precision Scientific Co.



16—Pipe Leak Clamps

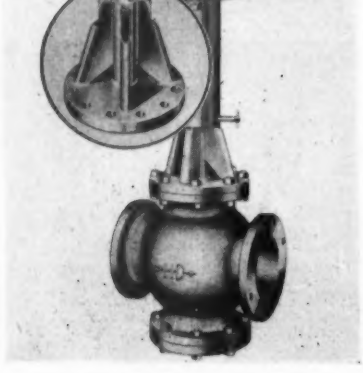


High pressure pipe leak clamps, available on a one week delivery basis, will withstand pressures up to 1100 psi on corroded pipe. Designed as permanent repair clamps for pipe leaks of oil, gas, aromatic fuels, water, etc., the stainless steel units weigh up to a maximum of only 6 lbs., and can be installed by one man. Features include laminated Hycar rubber pads which compress into the corroded area of pipe when under pressure, while resisting the tendency to cold flow; and a stainless steel patch plate which slides on the clamp band, affording proper positioning of clamp over leak. Available in all sizes for pipe from 2 to 8 in. Larger sizes on request. Marman Products Co., Inc.

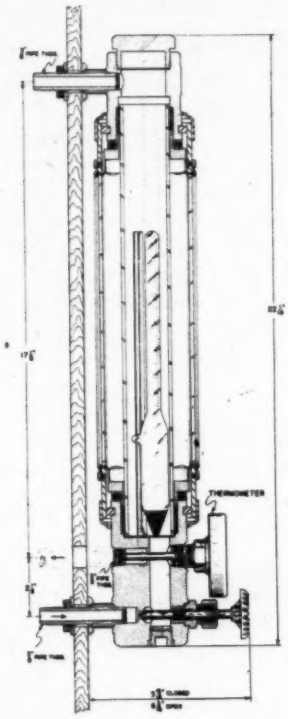
17—Fin-Cooled Valve

The Hammel-Dahl Vertical "U" type fin radiation bonnet has been designed for a complete line of diaphragm control valves in sizes 2 in. and larger. With the valve in the normal vertical position, the "U" section permits a natural draft which cools the packing box section when high temperature fluids are being handled.

Tests have indicated 35% better heat dissipation than with conventional horizontal fin designs, it is said. For example: with a common temperature of around 1000° F. on the body side of the bonnet, vertical fins will reduce the temperature to 235° F. at the packing box, while horizontal fins will permit a temperature of about 360°, regardless of the position of the valve. The valve is recommended for all applications where fluid temperature exceeds 450° F. or is below the freezing point. Hammel-Dahl Co.



18—Specific Gravity Tester



A new hydrometer-type specific gravity tester can be used for determining density of products, draw-offs, and slops from distillation columns. As shown in the sectional drawing, the liquid enters through the connection nearest the bottom, flows through the control valve, past a thermometer, and upward into a borosilicate glass tube containing the hydrometer. It then spills into two metal overflow tubes, from which it discharges through the connection just above the inlet. A special glass lug is blown on to the barrel of the hydrometer. The hydrometer is so placed that the lug projects between the two overflow tubes, preventing rotation of the hydrometer and maintaining visibility of its scale. Fischer & Porter Co.

19—Temperature Indicator

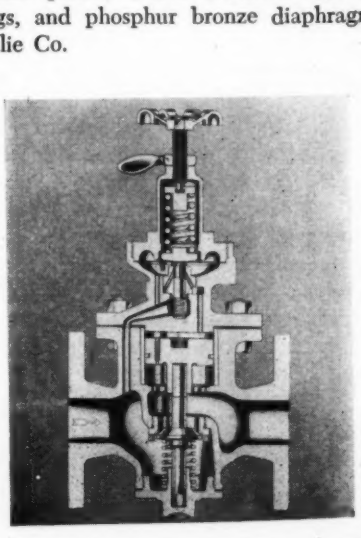
Where a large number of thermocouple temperatures must be logged in a short time, the Speedomax Indicator is said to fill the bill. To read a temperature, the operator flips a key switch marked for the desired thermocouple.

A single instrument can handle more

than 100 thermocouples. Key switches can be color-coded for convenience in identification. The indicator uses the same case as Micromax and Speedomax Recorders, and fits into standard panel cutouts for these instruments. All the more commonly used ranges for industrial thermocouples can be supplied. Leeds & Northrup Co.

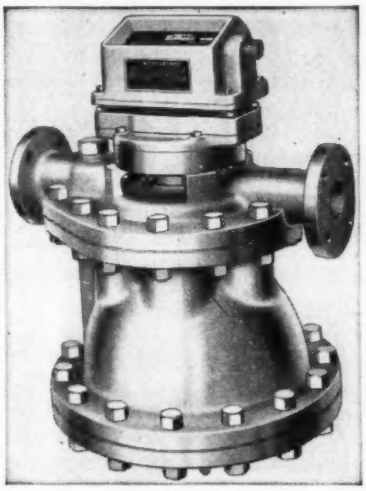
20—Unloading Valve

Throttling type unloading valve, class UL, for use with steam, air, or gas, is said to be applicable wherever a throttling type regulating valve is required to maintain a constant inlet pressure by relieving the excess to a lower pressure system. A feature of the operation is the smooth throttling control during the entire cycle of operation, combined with quick action under sudden pressure variations. Available in sizes from ½ to 4 in.; for inlet pressures from 25 to 300 psi, inlet temperatures to 550° F., and pressure differences not less than 15 psi. Construction features include high pressure bronze body, renewable wearing parts, hard surfaced seat ring, hardened stainless steel main and controlling valves, bronze piston, corrosion-resistant piston rings, and phosphur bronze diaphragm. Leslie Co.



21—Stainless Flow Meter

A new 1½ in., 50 gpm, flow meter is made of stainless steel for applications requiring such material to prevent corrosion, discoloration, or contamination. With a maximum working pressure of 250 psi, the meter incorporates vertical piston operation, minimizing cylinder and piston wear. The direction of flow keeps any suspended material flowing evenly in the meter. In design and principle of operation, it is basically similar to the Bowser Industrial Xacto meter. Bowser, Inc.



Trade Literature

22—Metallurgy Guide

Basic Guide to Ferrous Metallurgy, a 16¼ in. wide by 21 in. long, plastic-laminated wall chart, is an aid in heat-treating, processing, welding, and general fabrication of steels up to 0.9% carbon. It shows working characteristics at temperatures between −300 and + 2900° F. Temperature ranges are shown in 19 colors approximating the typical hot-body radiant hues. Includes definitions of 23 fundamental metallurgical terms and a diagram symbolizing the changes in grain size with temperatures. The Tempil Corp.

23—Laboratory Apparatus

Announcer of Scientific Equipment, a new house magazine emphasizing current developments in laboratory apparatus. Leading article in first issue describes the background and development of the modern analytical balance. Eberbach & Son Co.

24—Engine Lubrication

Marine Engine and Auxiliary Lubrication Vol. II, No. 1, of the Shell Panorama of Lubrication, is an 80-page booklet in color, describing and illustrating in considerable detail the fundamentals of lubricants and lubrication of marine and auxiliary engines and their accessories. Problems confronted in three major types of power plants—steam engines, steam turbines, and diesel engines—are covered. Shell Oil Co., Inc.

25—High-Pressure Processes

Superpressure Catalytic Hydrogenation Apparatus, an 88-page catalog (No. 406), includes a discussion of high-pressure processes, typical high-pressure flow sheets, and a detailed description of apparatus used in high-pressure and high-temperature technique, including pilot plants for many types of chemical syntheses, reaction vessels and shakers, valves, fittings, pumps, compressors, and instruments. American Instrument Co.

26—Deaeration Equipment

Cochrane Deaerators, Publication No. 3005 is a new 36-page catalog giving comprehensive treatment of tray-type deaerating heaters and deaerators, supplemented by discussions of atomizing deaerators for stationary and marine service, deaerating hot-water generators, cold water deaerators, and other degasification equipment. Five heat balance flow diagrams of actual installations are included. A special section explains metering deaerators equipped with V-notch recorders and electrical systems for remotely recording flow. A supplementary appendix on corrosion control is also included. Cochrane Corp.

27—New Cycling Plant

South Coles Levee Cycling Plant, a 32 page booklet in color, fully illustrated, describing the new Cycling Plant at South Coles Levee, Calif., operated by Ohio Oil Co. for the participating companies; Standard Oil Co. of California, Union Oil Co. of California Richfield Oil Corp., Tide Water Associated Oil Co., and Ohio Oil Co. A four-color stream-lined flow-sheet is included. The Fluor Corp.

For Your Convenience

Business reply cards are included in this issue of Petroleum Processing to assist you in obtaining more information on any of the items reviewed in "What's New!" You'll find them facing page 385. Just circle the numbers corresponding to the numbers on the items you're interested in, fill in the bottom of the card, and drop it in the mail. No postage required.

28—Steam Trap Maintenance

Tips on Trap Maintenance, a helpful article appearing in the Armstrong Trap Magazine, Vol. 16, No. 2, presents operating hints on the care of steam traps based on the experiences of one large user of this equipment. Also included in this issue is a chart for calculation of steam in lbs./min., pressure drop in psi, volume of steam in cu. ft./lb., and internal diameter of pipe in inches, for steam pipe design. Armstrong Machine Works.

29—Caustic Handling

Handling Caustics without Corrosion Problems, an 8-page bulletin giving comparative test data on Monel, 70/30 Copper-Nickel, mild steel, and other materials in refinery equipment handling caustic solutions. Includes service records of actual refinery operations in caustic regenerators for mercaptan removal units. International Nickel Co., Inc.

30—Caustic Soda

Columbia Caustic Soda, a 72-page booklet provides data on the two methods of manufacture and economics in the handling and use of various forms, solid, flake, 50% and 73% liquid. Photographs, charts, sketches and diagrams illustrate safe and efficient methods for shipping, receiving, and using caustic soda. Columbia Chemical Div., Pittsburgh Plate Glass Co.

31—Corrosion-Resistant Steel

Lukens Clad Steels, a recent revision of this bulletin is now available. It includes data explaining applications for Nickel-Clad, Inconel-Clad, and Monel-Clad steels for service in specific industries, classified according to the corrosive agent. Lukens Steel Co.

32—Synthetic Ammonia

Synthetic Ammonia Plants, N. E. C. Process, Bulletin No. A-101, a 14-page brochure including flow charts showing synthetic ammonia production from a variety of hydrogen sources—coke, hydrocarbon gases, or water electrolysis. Outlines of each phase of production, including gas purification, are included. Chemical Construction Corp.

33—Pressure Controllers

Engineering, Operating, and Maintenance Data on Pressure Controllers, External-Pilot-Operated, Bulletin No. 462, a 20-page illustrated booklet giving technical information on the design features of the control pilots and associated diaphragm regulating valves, including selection charts and capacity tables. Leslie Co.

Hydrocol Process Shows Many Improvements Not Found in the Fischer-Tropsch Synthesis

FRESH data on the Hydrocol process for the synthesis of natural gas into gasoline and other products indicate many applications in petroleum refineries not foreseen during the earlier development of this technique as an improvement over the Fischer-Tropsch synthesis.

Among probable new uses for the process is the conversion of fuel gas and/or heavy residua, from present processing operations, into more saleable products such as gasoline, kerosine, and gas oil. It is estimated that an additional 100,000,000 gals./yr. of gasoline could be produced by the synthesis of the present annual production of refinery gases.

These facts were brought out in a talk, "Synthetic Fuel Production by the Hydrocol Process," by P. C. Keith, president, Hydrocarbon Research, Inc., at the annual meeting of the Western Petroleum Refiners Assn., March 24-26, at San Antonio, Texas.

Hydrocol Not Fischer-Tropsch

The Hydrocol process is *not* the Fischer-Tropsch synthesis. This point is made early in the paper and stressed. The only common feature of the two processes is the use of carbon monoxide and hydrogen, it is said.

On the other hand, catalyst, synthesis temperature and pressure, means of securing synthesis mixture, and the design and operation of the reaction chamber are different. It is also stated that German developments were not of commercial interest or economically practical in this country.

The early part of the paper reviews the history of hydrocarbon synthesis from carbon monoxide and hydrogen, starting with Sabatier's work reported in 1902, its modification by German scientists to the production of industrial alcohol, and culmination in the Fischer-Tropsch synthesis plants investigated by the Allies at the end of World War II.

Cobalt Catalyst Is Expensive

Most serious faults of the German method which prevented it from being of commercial interest in the U. S. were: Expensive cobalt catalyst; inefficient preparation of synthesis mixture from coke; low temperature (400° F.)—atmospheric pressure reaction; inability to use by-product heat; limited throughput rate because of catalyst composition and size, coupled with reactor design; poor quality (40 motor octane) of synthetic gasoline and high manpower requirements.

The Hydrocol modification uses, first, a finely divided iron catalyst which costs about 5c/lb.; preparation of CO-H_2 reaction mixture by controlled combustion of natural gas (methane) with pure oxygen at 2250° F. and 350 psi; reaction at 250 psi and 600° F.; utilization of by-product heats of combustion and reaction heat by steam generation at 650 psi in quantities sufficient to operate all required utilities for synthesis; very high throughput rate (2000 cu. ft. synthesis gas per cu. ft. catalyst per hour) permitted by "fluid catalyst" operation which allows close temperature control and extraction of large amounts of heat, the limiting factors in German design, and a resultant gasoline of 65-67 clear Motor octane. Considered with poly gasoline, resulting from polymerization of olefinic gases produced during the synthesis, the overall motor fuel product rates 78-80 Motor octane clear (90-92 oct. Research).

The synthetic hydrocarbons are recovered from reactor gases identically to conventional extraction of natural gasoline by absorption, whence unreacted synthesis gases are compressed and recycled to the reactor. An additional refining step is required, however, to separate for further purification such oxygenated chemicals as formaldehyde, acetone and the like, which are also produced in the reaction.

No Unusual Corrosion

No unusual corrosion problems have been encountered in pilot plant work and none are expected in the two 6000 b/d plants to be constructed at Brownsville, Texas, and in the Hugoton, Kans., gas field. One barrel of synthesis product will require 10,000 cu. ft. of natural gas, including all fuel requirements.

The Hydrocol synthesis may have an extremely marked effect on the general philosophy of refining, this paper states. There is no technical reason why a Hydrocol plant cannot utilize a mixture of natural and refinery gases, or these gases and refinery residua; coal or crude oil also may be used as a source for synthesis gas. On the one hand the process puts a ceiling on the maximum price which can be charged for crude oil or gas above which gasoline synthesized from coal can compete economically; on the other it solves the question of what raw material will be used to make gasoline and fuel oil when reserves of crude and gas become depleted.

The process also offers a means of utilizing present refinery by-products, such as fuel gas and heavy residua. The three products from refining of crude which constitute the "money crop" are, of course, gasoline, kerosine and gas oils. Gases and heavy fuel oils, including pitch, are relatively unprofitable or complete losses. It is stated that a refiner could run his unsalable gas through a Hydrocol plant—assuming his refinery is sufficiently large to make such a unit profitable—and produce an excellent gasoline plus more gas oil and chemicals. Heavy residua or pitch would be used instead of gas as refinery fuel. This would permit releasing cut-back gas oil, customarily blended with pitch, for sale as a higher-grade fuel oil. It is estimated that if all refinery gas produced annually in this country were synthesized to gasoline by the Hydrocol process, an additional 100,000,000 gal. per year would be realized.

Can Improve Product Quality

The Hydrocol process also may prove a potential competitor of catalytic cracking, since it is the only one besides polymerization or alkylation which can convert refinery wastes to valuable products. Likewise it offers the refiner means of increasing product quality simultaneously with product quantity, whereas more conventional processes do not. A synthesis plant costs more than a catalytic cracking unit but the charge stock is much less expensive. Also, the large quantities of olefins produced in the synthesis may permit the economical inclusion of alkylate as a blending agent in ordinary motor fuel.

Making gasoline from coal by the Hydrocol process is not impossible, said Mr. Keith, and may come by 1951. A ton of coal will produce 1.78 bbls. of synthetic oil, including all fuel necessary for the synthesis.

At $1.25 per ton—a not impossible figure because sizing and washing operations would be eliminated and it might be more feasible to gasify coal in place—a synthetic crude oil can be produced for 70c/bbl. The value of the products from such a crude will aggregate about $2.25/bbl.

Pay Off Plant in Five Years

Under these conditions, an investor could afford to spend $4250 per daily bbl, and pay off the plant in five years. Investment costs in a present-day 10,000 bbl. refinery amount to $4200/bbl.

In the discussion following Mr. Keith's paper, it was stated that the smallest economically feasible hydrocol plant would probably approximate 3500 b/d. Plants much larger than 6000 b/d are also entirely practicable. Distillate produced by the process is 39 to 40 gravity, and rates between 50 and 75 Cetane number.

PERCO CYCLOVERSION For The Small Refiner

Presented before the 44th semi-annual meeting of the National Petroleum Assn., Cleveland, April 17, 1947.

By V. W. DANIELS and M. W. CONN
Perco Division, Phillips Petroleum Co.

The catalytic desulfurization and catalytic reforming phases of Perco Cycloversion offer means for improving the octane quality of thermally cracked, straight-run and natural gasolines produced from existing equipment, with a minimum of additional investment and operating charges. Data is given on characteristics of raw and treated stocks of various types, from both commercial and pilot plant operations, to show the degree of improvement in clear and leaded octane numbers, by both ASTM and Research Methods.

Desulfurization of the separate streams or a blend of total refinery gasoline of either nominally high or low total sulfur content will result in considerable octane improvement at substantially no volume loss. Since both operations are performed in the same equipment, further octane improvement may be realized over that obtained by desulfurization only, by raising the temperature of operations to catalytic reforming conditions. In refineries with catalytic cracking facilities, the desulfurization and reforming operations are applicable in upgrading the low octane gasoline from straight distillation to improve the qualities of the total gasoline product.

THERE is at present a very wide discrepancy between refineries in the maximum octane rating of fuels that can be produced. This situation is partly due to the war years when many refiners, mostly the majors or larger companies, made numerous installations such as catalytic cracking, alkylation, isomerization, etc., for the production of tremendous quantities of war time fuels, with little or no economic considerations. As a result, refineries now may or may not be classified as "modern" depending upon whether or not they have these catalytic facilities to enable them to keep pace with the octane parade. This great diversity in processing facilities has created a condition or problem not normally encountered in the peace-time development of the petroleum refining industry.

This problem may be solved by either of the two methods of approach. The first involves the installation of new and expensive catalytic cracking and auxiliary facilities which are usually and except for abnormal conditions beyond the reach of the small refiner. The other solution is the improvement in quality of products normally produced from present equipment with a minimum of additional investment and operating charges.[1]

Much has been said and published on the various catalytic cracking processes.[2,3] The present paper is concerned primarily with means of improving the quality of presently produced products which, in some cases, result in overall refinery octane improvements greater than can otherwise be obtained by the much more expensive catalytic cracking installations. The term Perco Cycloversion ordinarily embraces catalytic gas-oil cracking, catalytic desulfurization and catalytic reforming.[4,5,6] Only the last two named processes will be discussed in this paper.

The Perco catalytic desulfurization and catalytic reforming processes are the outgrowth of investigations dating back several years seeking a practical and economic means of octane number upgrading of thermally cracked, straight-run and natural gasolines. These processes offer economically sound approaches to the problem and are based on the maximum use of existing refining facilities and a minimum of additional equipment, resulting in comparatively low capital expenditures.

Catalytic Desulfurization

The advent of tetraethyl lead as an antiknock agent emphasized adverse effects of sulfur compounds on the octane rating of automotive and aviation fuels. Investigations by Schulze and Buell[7] showed that wide deviations in the octane ratings and TEL susceptibilities of some straight-run gasoline were attributable in a large degree to sulfur compounds. This explanation has received verification by others in the petroleum-refining industry and now is generally accepted.

The Perco catalytic desulfurization process is a catalytic means of decomposing organic sulfur compounds in light oils to hydrogen sulfide, in which form the sulfur may be easily removed by any one of several conventional methods. The bauxite catalyst employed readily decomposes mercaptans, alkyl sulfides, and alkyl disulfides to hydrogen sulfide. Thiophenes constitute the only important class of sulfur compounds not greatly affected. Fortunately the thiophenes are the least objectionable with respect to effect on tetraethyl lead response.

Catalytic desulfurization of straight-run stocks results in no appreciable change in the composition of the treated product other than the reduction of sulfur content. However, with cracked gasolines the octane improvement cannot in all cases be attributed to "desulfurization" alone. Polymerization of gum forming constituents and side reactions that further enhance the octane number improvement may also occur. The absence of undesirable side reactions in the catalytic treatment is indicated by the fact that there is no appreciable change in physical properties such as vapor pressure, gravity or distillation characteristics. Clear octane number improvements of the order of three or more numbers are often obtained. The greatest advantage of catalytic desulfurization, however, results from the increased leaded octane numbers, which with straight-run stocks may amount to 10 or more numbers.

Experimental investigations of recent years conducted in pilot plants and operation of commercial units have proven conclusively these features of catalytic desulfurization on a rather wide variety of stocks.

Straight-Run Gasolines — Straight-run gasolines respond readily to catalytic desulfurization. Specific examples of commercial plant desulfurization on stocks of this type are of interest in that they illustrate normal operating conditions and results. Data on straight-run gasolines of rather high sulfur contents are presented in Table 1. The straight-run stock at Plant "A" was catalytically desulfurized at 710° F. The reduction of total and mercaptan sulfur contents amounted to 86 and 82 wt. % respectively. In addition to a clear octane improvement of 1.7 numbers, the response

TABLE 1—Commercial Results—Perco Catalytic Desulfurization of High-Sulfur Content Straight-Run Gasolines

Unit Designation, Capacity	Plant "A", 5000 B/D			Plant "B", 300 B/D			Plant "C", 3000 B/D		
Location	—West Texas—			—Michigan—			—Mid Continent—		
Crude Source	Lea-Ward-Eddy						Mixed		
Operation	Desulfurization			Desulfurization			Desulfurization		
	Charge	Product	Gain	Charge	Product	Gain	Charge	Product	Gain
Inspection Data:									
ASTM Octane, Clear	57.5	59.2	1.7	36.4	41.6	5.2	57.9	61.3	3.4
Plus 1 cc. TEL/Gal.	63.6	68.3	4.7	42.6	54.0	11.4	...	...	...
Plus 3 cc. TEL/Gal.	70.7	76.0	5.3	52.4	68.5	16.1	71.2	81.0	9.8
Total Sulfur, wt. %	0.152	0.020	...	0.169	0.005	...	0.114	0.031	...
Mercaptan Sulfur, wt. %	0.028	0.005	...	0.104	Sweet	...	...	...	...
RVP, Psig. @ 100°F.	7.2	7.2	...	6.3	6.8	...	...	...	...
Gravity, °API @ 60°F.	57.7	57.7	...	65.8	65.5	...	66.1	67.0	...
ASTM Distillation, °F.									
First Drop	103	106	...	112	110	...	84	96	...
5% Evaporated	...	...	...	148	143	...	...	...	...
10% Evaporated	168	170	...	164	162	...	146	155	...
20% Evaporated	196	196	...	184	183	...	176	182	...
50% Evaporated	254	252	...	221	223	...	235	240	...
70% Evaporated	...	...	...	243	245	...	...	...	...
90% Evaporated	334	328	...	273	279	...	310	314	...
95% Evaporated	...	...	...	288	301	...	342	348	...
End Point	390	391	...	344	383	...	368	372	...
Recovery, %	98.0	98.0	...	99.1	98.9	...	...	...	...
Residue, %	1.0	1.0	...	0.3	0.5	...	...	...	...
Operating Conditions:									
Chg. Rate, Bbls./Ton/Day		290			200			155	
Barrels Treated/Ton		524			...			3521	
Bauxite Catalyst, Tons		17			1.37			10.5	
Temperature, °F.		710			770			850	
Pressure, Psig.		...			40			95	

TABLE 2—Perco Catalytic Desulfurization of Blended Gasolines

Unit Designation, Capacity	Commercial Plant "D" 2000 B/D					Pilot Plant Data		
Crude Source	—Michigan—					Mid-Continent		
Stock	Raw	Desulf.	Gain	Desulf.	Gain	Raw	Desulf.	Gain
Inspection Data:								
Astm Octane, Clear	58.6	63.9	5.3	63.2	4.6	59.9	61.6	1.7
Plus 1.0 cc. TEL/Gal.	66.4	73.9	7.5	72.7	6.3	67.4	70.7	3.3
Plus 3.0 cc. TEL/Gal.	73.1	79.0	5.9	78.9	5.8	73.8	77.2	3.4
Research Octane, Clear	61.4	67.2	5.8	66.2	4.8	61.0	61.7	0.7
Plus 1.0 cc. TEL/Gal.	70.0	76.6	6.6	75.3	5.3	71.0	72.6	1.6
Plus 3.0 cc. TEL/Gal.	77.9	83.7	5.8	82.9	5.0	78.3	80.8	2.5
Total Sulfur, wt. %	0.088	0.024	...	0.023	...	0.070	0.031	...
Mercaptan Sulfur, wt. %	0.023	Sweet	...	0.001	...	0 024	0.003	...
RVP Psig. @ 100° F.	9.9	10.0	...	12.1	...	8.3	8.2	...
Gravity, °API @ 60° F.	66.2	65.9	...	67.7	...	61.2	60.9	...
ASTM Distillation, F.								
First Drop	94	81	...	88	...	94	97	...
5% Evaporated	113	101	...	99	...	125	131	...
10% Evaporated	128	120	...	116	...	142	144	...
20% Evaporated	152	146	...	142	...	172	175	...
50% Evaporated	212	210	...	207	...	250	252	...
70% Evaporated	248	247	...	243	...	300	300	...
90% Evaporated	295	296	...	293	...	353	356	...
95% Evaporated	320	320	...	317	...	374	375	...
End Point	355	385	...	356	...	394	409	...
Recovery, %	97.5	96.0	...	96.5	...	97.2	97.8	...
Residue, %	0.5	0.8	...	0.4	...	1.0	1.0	...
Operating Conditions:								
Chg. Rate, Bbls./Ton/Day	.....	153	...	173	...	.....	188	...
Barrels Treated/Ton	.....	55	...	930	...	.....	.....	...
Bauxite Catalyst, Tons	.....	2.35	...	2.35	...	.....	.....	...
Top Catalyst Temp., F.	.....	732	...	798	...	.....	770	...
Pressure, Psig.	.....	42	...	38	...	.....	35	...

to 3.0 cc. TEL was increased from 13.2 to 16.8 numbers on the product from this operation.

The treatment of the low end point, low octane and high sulfur straight-run gasoline from Michigan crude, Plant "B," indicates the results to be obtained on similar type materials. A reduction of 96 wt. % of total sulfur was effected in this instance and virtually complete removal of mercaptan sulfur, as indicated by the "sweet" product, was obtained. The improvement was 5.2 ASTM unleaded octane numbers and the lead response was increased from 16 numbers for the raw charge to 27.9 on the treated stock.

Treatment of Plant "C" high sulfur straight-run gasoline at a somewhat lower space velocity and a temperature of 850° F. effected a total sulfur reduction of 71 wt. %. It is apparent that the type of sulfur compounds contained in this straight-run fraction are relatively refractory; nevertheless, a net increase of 3.4 octane numbers clear and 9.8 numbers at 3.0 cc. TEL/Gal. was observed.

Blended Gasolines—Table 2 presents typical results from the catalytic desulfurization of cracked and straight-run blends containing less than 0.10% total sulfur. The charge to the Plant "D" desulfurization unit comprised approximately a 50/50 blend of straight-run and Dubbs-cracked gasoline from Michigan crude. This catalytic treatment was continued for six days with a total throughput of about 1000 bbl. per ton of catalyst. To compensate for catalyst activity decline due to carbon deposition, the reactor outlet temperature was gradually increased from 725° to 790° F. This type of operation resulted in rather uniform total sulfur reduction of approximately 73 wt. %.

It is apparent from the vapor pressure measurements that the high temperature of operation resulted in possibly some mild reforming of this stock; however, there is no other appreciable change in the character of the treated products. The caustic-washed product was sweet to the doctor test. It will be noted that the octane rating of the catalytically treated product containing 1 cc. TEL is about the same as the undesulfurized gasoline with 3 cc. TEL.

Another illustration of octane appreciation of blended gasoline is given under some typical pilot plant data in Table 2. This Mid-Continent gasoline blend was approximately 40% thermal cracked-poly mixture and 60% straight-run and contained only 0.07% total sulfur. This blend, except for varying seasonal natural gasoline requirements, represents the total refinery gasoline. A full 3 ASTM octane numbers is realized at an average of 2 cc. TEL/Gal. and no volume losses other than handling or mechanical losses were incurred.

Catalytic Reforming

The normal benefits derived from catalytic desulfurization are obtained in the Perco catalytic reforming operation together with an appreciable increase in clear octane rating due to some additional mild cracking or reforming. The latter is evidenced by the production of fixed gases and increasing hydrocarbon destruction with increasing severity of operating conditions.

Straight-Run Gasolines—Typical results for the catalytic reforming of various straight-run stocks from a broad range of crude oils are presented in Tables 3 to 5. Table 3 represents pilot plant data for the Perco catalytic reforming of an Illinois straight-run naphtha prepared by the preliminary fractionation of the full-range gasoline yielding 10.6% C_4 and lighter from debutanization and a light overhead fraction of 41.4% of the sample as received. The residual portion, representing 48.0% of the full-range material was the reformer charging stock. This naphtha was subjected to two different tests at destruction levels giving 2.43 and 4.83 wt. % of dry gas (C_2 and lighter) based on the 242-368° F. ASTM range naphtha charged at 1010° and 1030° F., respectively.

Calculations were made for blends based upon the recombining of the reformed products from each test with (a) the light overhead fraction, (b) the equivalent polymer gasoline available from the C_3 and C_4 olefins produced in the reforming operation and (c) added butanes to 10 lb. Reid vapor pressure. These two operations realized yields of 97 and 94.6% of the full-range as received having ASTM octane numbers of 80.2 and 81.8 respectively at 3 cc. TEL/Gal. as compared to 73 on the raw stock with a like increment of tetraethyl lead.

The results from the pilot plant catalytic reforming of a debutanized low-sulfur, low-octane, Mid-Continent straight-run gasoline from Oklahoma crude are presented in Table 4. This

If...

supported catalysts grew on trees — with the perfect one yours for the picking—how simple it would be. But they don't! Almost always there are hurdles to clear—problems to sweat out. As we see it (and practice it, too) such factors as helpful technical information from our men, purity and efficiency of our carrier, special facilities at our plant—all, are vital aids to you in arriving, finally, at *the right* catalyst.

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TABLE 3—Pilot Plant—Perco Catalytic Reforming Illinois Straight-Run Naphtha

	Full Range As Rec'd.	Debutanized Overhead Fraction	Reformer Charge	Test No. HL-1-1 Reformer Effluent	Blend No. 1*	Test No. HL-2-1 Reformer Effluent	Blend No. 2*
Yield Summary, Per Cent of Charge							
Dry Gas (C_2 and lighter), Wt. %	.....	.....	.....	2.43	.....	4.83	.....
Propylene, Vol. %	.....	.....	.....	1.53	.....	3.00	.....
Total Propylene-Propane, vol. %	.....	.....	.....	3.25	.....	4.91	.....
Butylenes, vol. %	.....	.....	.....	1.00	.....	2.97	.....
Total Butylenes-Butanes, vol. %	.....	.....	.....	1.57	.....	3.96	.....
Debutanized Gasoline, vol. %	.....	.....	.....	93.85	.....	87.78	.....
Carbon, wt. %	.....	.....	.....	0.18	.....	0.33	.....
Inspection Data:							
ASTM Octane, Clear	54.1	62.4	36.7	45.6	57.6	52.6	61.3
Plus 1.0 cc. TEL/Gal.	64.7	75.2	47.3	59.0	70.5	63.9	73.1
Plus 3.0 cc. TEL/Gal.	73.0	83.4	59.4	70.8	80.2	73.8	81.8
Research Octane, Clear	52.7	64.8	33.8	47.8	60.1	54.6	63.8
Plus 1.0 cc. TEL/Gal.	64.2	75.5	44.8	61.0	71.8	.....	.....
Plus 3.0 cc. TEL/Gal.	74.2	83.8	58.8	72.4	81.3	76.4	83.4
Total Sulfur, wt. %	0.022	.....	.....	0.008	.....	.....	.....
RVP, Psig. @ 100° F.	10.1	7.2	0.8	1.3	10.0	1.7	10.0
Gravity, °API @ 60° F.	64.4	70.6	54.7	54.5	.....	54.3	.....
ASTM Distillation, °F.							
First Drop	91	111	242	175	.....	149	.....
5% Evaporated	112	133	257	230	.....	217	.....
10% Evaporated	140	141	263	250	.....	235	.....
20% Evaporated	172	151	269	264	.....	254	.....
50% Evaporated	236	174	289	288	.....	283	.....
70% Evaporated	274	190	305	305	.....	300	.....
90% Evaporated	313	211	331	332	.....	329	.....
95% Evaporated	333	223	341	344	.....	342	.....
End Point	362	268	368	394	.....	388	.....
Recovery, %	96.8	98.1	99.0	99.0	.....	98.9	.....
Residue, %	0.4	0.5	0.3	0.5	.....	0.6	.....
Operating Conditions:							
Flow Rate, Bbl./Ton/Day	.....	.....	.....	290	.....	290	.....
Top Catalyst Temperature, °F.	.....	.....	.....	1010	.....	1030	.....
Pressure, Psig.	.....	.....	.....	50	.....	50	.....
Yield, vol. % Full Range as Rec'd.	100.0	41.4	48.0	45.1	97.0	42.2	94.6
Composition of Blend, vol. %							
Debutanized Overhead Fraction	.....	.....	.....	.....	42.7	.....	43.7
Reformed C_5+Gasoline	.....	.....	.....	.....	46.5	.....	44.6
Poly Gasoline	.....	.....	.....	.....	0.8	.....	2.0
Butanes	.....	.....	.....	.....	10.0	.....	9.7
Total	.....				100.0		100.0

* Calculated Data.

TABLE 4—Pilot Plant—Perco Catalytic Reforming of Mid-Continent (Okla.) Straight-run Gasoline

	Full Range As Rec'd	Test No. HX-1-1 Debut. Charge	Debut. Product	Blend Product Poly Gasoline(1)	Blended Product, Poly Gasoline and Butanes(1)
Yield Summary, Per Cent of Charge:					
Dry Gas, (C_2 and Lighter), wt. %	...	...	8.3	...	...
Propylene, vol. %	...	...	6.0	...	...
Total Propylene-Propane, vol. %	...	...	8.2	...	...
Butylenes, vol. %	...	...	4.5	...	...
Total Butylenes-Butanes, vol. %	...	...	5.4	...	...
Debutanized Gasoline, vol. %	...	...	80.2	...	...
Carbon, wt. %	...	...	0.5	...	...
Inspection of Gasoline Fractions:					
ASTM Octane, Clear	50.2	45.0	61.6	64.1	66.8
Plus 1.0 cc. TEL/Gal.	62.8	58.2	71.8	73.5	76.5
Plus 3.0 cc. TEL/Gal.	73.3	69.2	78.2	79.4	82.5
Research Octane, Clear	48.1	43.6	64.6	67.4	70.2
Plus 1.0 cc. TEL/Gal.	59.5	56.2	73.8	75.9	78.9
Plus 3.0 cc. TEL/Gal.	73.9	69.8	82.6	84.0	86.8
Total Sulfur, wt. %	...	0.018	0.008	...	...
Mercaptan Sulfur, wt. %	...	0.003	0.002	...	...
Bromine Number	Negl.	Negl.	20	...	...
RVP Psig. @ 100°F.	9.6	2.8	3.6	3.5	9.6
Gravity, °A.P.I. @ 60°F.	62.4	59.1	57.2	...	...
ASTM Distillation, °F.					
First Drop	97	141	130	...	...
5% Evaporated	117	171	161	...	...
10% Evaporated	148	188	177	...	...
20% Evaporated	182	206	194	...	...
50% Evaporated	248	261	248	...	...
70% Evaporated	290	299	288	...	...
90% Evaporated	346	359	347	...	...
95% Evaporated	368	381	374	...	...
End Point	407	408	415	...	...
Recovery, %	96.2	98.9	98.8	...	...
Residue, %	0.8	0.2	0.7	...	...
Operating Conditions:					
Flow Rate, Bbl./Ton/Day	...	...	335	...	...
Top Catalyst Temperature, °F.	...	...	1014	...	...
Pressure, Psig.	...	...	50	...	...
Yield, vol. % Full Range As Rec'd.	100.0	89.4	71.7	77.8 vol. gal.(2)	87.1 vol. gal.(2)
Composition of Blend:				%	%
Reformed Debutanized Gasoline	...	...	...	92.2 71.7	82.3 71.7
Poly Gasoline	...	...	...	7.8 6.1	7.0 6.1
Butanes	...	...	...	... ...	10.7 9.3
Total	...	...	...	100.0 77.8	100.0 87.1

(1) Calculated data.

(2) Based on 100 gallons of gasoline as received.

test performed at 1014° F. top catalyst bed temperature and a liquid space velocity of 335 bbl. of gasoline per ton of catalyst per day, gave a yield of 82.2% of charge with ASTM and Research clear octane improvements amounting to 16.4 and 21 points respectively. The octane appreciations represented by the reformed product are considerably above those normally obtained in a desulfurizing treatment of such a stock.

A calculated blend containing the C_5+ reformed gasoline, equivalent poly from C_3—C_4 reformer olefin production and sufficient butanes to give a Reid vapor pressure equal to that of the material as received gives an 87.1% yield of gasoline having an engine rating of 76.5 ASTM octane number at the 1 cc. TEL level which is 3.2 units higher than the 3 cc. leaded rating of the untreated material. The ASTM and Research 3 cc. leaded ratings calculate 82.5 and 86.8 octane numbers, respectively, compared to corresponding values of 73.3 and 73.9 numbers for the raw full range gasoline as received.

Typical results to be expected in catalytic reforming to a rather shallow depth of conversion on a straight-run gasoline from a Pennsylvania-type crude oil are illustrated in Table 5. It is noted that the raw gasoline charged to the pilot plant operation contained 1.1% propane, 4.4% butanes and 94.5% of C_5 and heavier. The debutanized reformed gasoline from this test, performed at 1015° F. and a rate of 260 bbls./ton/day, amounted to 88.9% of the total reformer charge. On the basis of C_5+ in the

TABLE 5—Pilot Plant—Perco Catalytic Reforming Pennsylvania Straight-Run Gasoline

	Reformer Charge	Reformer Product
Yield Summary, Per Cent of Charge		
Dry Gas (C_2 and Lighter), wt. %		4.50
Propylene, vol. %		2.85
Total Propylene - Propane, vol. %		4.83
Butylenes, vol. %		3.18
Total Butylenes-Butanes, vol. %		3.85
Debutanized Gasoline, vol. %		88.90
Carbon, wt. %		0.16
Unaccounted, wt. %		0.12
ASTM Octane, Clear	48.8	61.5
Plus 1.0 cc. TEL/Gal.	57.3	71.0
Plus 2.0 cc. TEL/Gal.	63.3	77.2
Plus 3.0 cc. TEL/Gal.	67.1	79.6
Research Octane, Clear	49.6	65.8
Plus 1.0 cc. TEL/Gal.	57.9	74.4
Plus 2.0 cc. TEL/Gal.	64.5	80.8
Plus 3.0 cc. TEL/Gal.	68.7	83.5
Total Sulfur, wt. %	0.055	0.005
RVP Psig. @ 100°F.	8.5	10.2
Gravity, API @ 60°F.	62.2	62.8
Bromine Number	Negl.	23
ASTM Distillation, °F.		
First Drop	100	88
5% Evaporated	130	109
10% Evaporated	156	137
20% Evaporated	193	173
50% Evaporated	262	248
70% Evaporated	306	289
90% Evaporated	353	343
95% Evaporated	370	363
End Point	404	409
Recovery, %	96.9	96.0
Residue, %	0.6	0.5
Operating Conditions:		
Flow Rate, Bbl./Ton/Day		260
Top Catalyst Temp., °F.		1015
Pressure, Psig.		50

charge, the corresponding gasoline yield is 94.1%. The 61.5 and 79.6 octane numbers for the clear and 3 cc. leaded ASTM ratings represent appreciations of 12.7 and 12.5 points, respectively. It will be noted in this, as well as other tests, that even more improvement in Research ratings than in ASTM ratings are obtained.

The above discussions regarding gasoline quality and octane improvement by either the catalytic desulfurizing or reforming processes, have been primarily concerned with the treatment of straight-run stocks or a blend of straight-run and cracked materials. The data of Table 6 is indicative of the appreciation to be realized on total refinery gasoline blends by catalytic treatment of the component streams in "blocked out" operations. These stocks are from a refinery processing a North-Central Texas crude oil. The low-sulfur, relatively high octane light straight run gasoline, representing 37.5% of the gasoline production, was not subjected to catalytic treatment but was used "as received" in the preparation of the blends shown in the subject table. The sample of heavy straight-run naphtha, amounting to 17.9% of total gasoline, was catalytically reformed in the pilot plant at 1000° F. and 235 b/ton/day to yield a debutanized product having excellent ASTM and Research appreciations.

By the respective test methods the improvements at 3 cc. leaded ratings are 15.5 and 22.8 octane numbers. The 44.6% cracked gasoline fraction containing 0.225% sulfur was subjected to a desulfurizing treatment at conventional operating conditions for such a stock. The 1 cc. leaded ratings by both the ASTM and Research test methods on the desulfurized material indicates TEL savings of approximately 2 cc. per gal. when compared to the desulfurizer charge. A composite refinery gasoline blend containing the untreated light straight-run gasoline and the products from the two catalytic treatments represents a recovery of 97.4 vol. % based on the materials as received, and a gain of 4 ASTM octane numbers when leaded to 3 cc. TEL/gal.

Blended Gasolines—Table 7 compares the results of pilot plant catalytic desulfurizing and reforming operations on blended gasolines from a Mid-Continent (Kansas) crude oil. Desulfurization at the indicated operating conditions of the blend designated as Sample "A" resulted in an octane number appreciation at the 3 cc. TEL level of 3.4 ASTM octane numbers with a 2.1 increase in Research rating at the same level. Sample "B," the charge to the reforming operation, is identical with "A" except that it contains no poly gasoline. After debutanizing, this material was catalytically reformed at 990° F. and a flow rate of 240 b/ton/day. The C_5+ gasoline from this operation had an ASTM clear octane rating of 65.8, or an improvement

TABLE 6—Pilot Plant—Perco Catalytic Treatment of North-Central Texas Gasoline Stocks

Stock:	Light St. Run Gaso.	Heavy Straight Run Naphtha		Cracked Gasoline			
Type Treatment:		Reforming		Desulfurization			
Sample Designation:		Charge	Product	Charge	Product	Refinery Blends(3)	
Test Designation:		HRG-1-1	HRG-1-1	HDE-1-1	HDE-1-1	Raw	Treated
Field Summary, Per Cent of Charge					99.5		
Dry Gas (C_2 and lighter), wt. %			5.07				
Propylene, Vol. %			3.56				
Total Propylene-Propane, vol. %			6.40				
Butylenes, vol. %			2.59				
Total Butylenes-Butanes, vol. %			3.96				
Debutanized Gaso., vol. %			86.76				
Carbon, wt. %			0.70				
ASTM Octane, Clear	59.4	29.4	53.0(1)	65.9	68.5	59.2	62.6
Plus 1.0 cc. TEL/Gal.	71.6	41.6	63.7	70.4	73.5	67.2	70.2
Plus 3.0 cc. TEL/Gal.	79.7	56.6	72.1	73.8	77.3	73.6	77.5
Research Octane, Clear	59.0	33.0	58.7	72.2	75.6	62.5	67.0
Plus 1.0 cc. TEL/Gal.	69.3	42.2	66.8	78.4	82.4	70.2	74.9
Plus 3.0 cc. TEL/Gal.	80.2	55.2	78.0	82.8	87.3	78.3	81.2
Total Sulfur, wt. %	0.015	0.024	...	0.225	0.178	0.109	0.084
Mercaptan Sulfur, wt. %	0.000	0.001	...	0.011	0.000	0.003	...
Doctor Test	Sweet	Sl. Sour	Sl. Sour	Sour	Sweet	Sour	Sl. Sour
Bromine Number	Negl.	Negl.	19	61	61	27	28
Gravity, °API @ 60°F.	66.4	48.5	47.9	56.3	56.0	58.0	57.3
RVP, Psig.° 100°F.	10.6	0.3	1.4	6.1	6.8	7.3	7.6(2)
ASTM Distillation, °F.							
First Drop	91	301	140	105	101	100	107
5% Evaporated	107	318	213	134	136	132	145
10% Evaporated	131	325	261	158	160	155	167
20% Evaporated	160	331	302	191	191	190	198
50% Evaporated	218	342	335	269	267	266	270
70% Evaporated	248	351	348	311	312	310	311
90% Evaporated	287	369	369	365	365	355	365
95% Evaporated	303	383	387	381	384	373	385
End Point	347	417	437	401	447	398	427
Recovery, %	96.5	98.2	98.2	97.5	97.5	97.5	98.5
Residue, %	0.5	0.8	1.0	0.8	1.0	1.0	0.5
Operating Conditions:							
Flow Rate, Bbl./Ton/Day			235		195		
Top Catalyst Temperature, °F.			1000		758		
Pressure, Psig.			50		35		
Composition of refinery Blends, vol. % (Based on 100 gallons raw composite)							
Light Straight Run Gasoline						37.5	37.5
Heavy Straight Run Naphtha						17.9	15.5
Cracked Gasoline						44.6	44.4
Catalytic Treating Losses						...	2.6
						100.0	100.0

(1) Inspection tests made on debutanized gasoline.
(2) Calculated Value.
(3) The light straight-run gasoline used in preparation of raw and treated blends received no catalytic treatment.

TABLE 7—Pilot Plant—Perco Catalytic Treatment Mid-Continent (Kansas) Blended Gasolines

Type of Operation:	Desulfurizing		Reforming		Blend
Sample Designation:	Sample "A"	Sample "A"	Sample "B"	Sample "B"	Reformed "B" with
Test Designation:	HDA-1-1	HDA-1-1	HRA-1-1	HRA-1-1	Poly Gasoline
Stock Designation:	Charge	Product	Charge*	Product	and Butanes
Composition, Volume Per Cent:					
Straight-Run Gasoline	60.4	.....	62.9	.....	.....
Cracked Gasoline	35.6	.....	37.1	.....	.....
Poly Gasoline	4.0	.....	.....	.....	8.2
Reformed C_5 + Gasoline "B"	.....	.....	.....	.....	81.8
Added Butanes	.....	.....	.....	.....	10.0
	100.0		100.0		100.0
Yield Summary, Per Cent of Charge:					
Dry Gas (C_2 and lighter), wt, %	.....	.....	.....	4.3	.....
Propylene, vol. %	.....	.....	.....	3.4	.....
Total Propylene-Propane, vol. %	.....	.....	.....	5.1	.....
Butylenes, vol. %	.....	.....	.....	3.0	.....
Total Butylenes-Butanes, vol. %	.....	.....	.....	4.0	.....
Debutanized Gasoline, vol. %	.....	.....	.....	86.9	.....
Carbon, wt. %	.....	0.14	.....	0.7	.....
ASTM Octane, Clear	64.0	65.3	59.6	65.8	70.8
Plus 1.0 cc. TEL/Gal.	71.8	74.7	68.4	73.9	78.8
Plus 3.0 cc. TEL/Gal.	77.9	81.3	75.6	79.5	83.6
Research Octane, Clear	66.9	68.2	63.2	70.2	75.3
Plus 1.0 cc. TEL/Gal.	75.2	76.6	71.4	79.2	83.6
Plus 3.0 cc. TEL/Gal.	82.9	85.0	81.2	85.1	88.8
Total Sulfur, wt. %	0.036	0.023	0.039	0.031	.....
Mercaptan Sulfur, wt. %	0.007	0.002	.....	0.005	.....
Bromine Number	27	31	24	31	.....
Gravity, °API @ 60° F.	65.0	64.7	61.7	60.4	64.7
Reid Vapor Pressure, Psig. @ 100° F.	9.5	9.4	4.4	4.7	10.6
ASTM Distillation, °F.					
First Drop	93	93	121	115	91
5% Evaporated	109	108	152	142	104
10% Evaporated	126	126	162	152	118
20% Evaporated	152	153	178	168	141
50% Evaporated	217	217	228	216	210
70% Evaporated	257	258	269	256	252
90% Evaporated	326	332	339	332	329
95% Evaporated	361	364	369	371	367
End Point	396	426	403	417	419
Recovery, %	97.1	97.0	98.0	98.0	97.0
Residue, %	0.9	0.8	1.0	1.0	0.8
Yield, vol. % Sample "A":	100	99.5†	87.6	76.1	92.9
Operating Conditions:					
Top Catalyst Temperature, °F.	.....	760	.....	990	.....
Pressure, Psig.	.....	35	.....	50	.....
Flow Rate, Bbl./Ton/Day	.....	235	.....	240	.....
Duration, Hours	.....	24	.....	24	.....
Catalyst (Cyclocel Grade)	.....	Bauxite	.....	Bauxite	.....

* Sample "B" was debutanized prior to reforming operation.
† Estimated maximum 0.5% handling loss.

of 6.2 numbers over the charge, as compared to only 1.3 units improvement in ASTM clear rating for the desulfurizing operation.

A blend containing the C_5+ gasoline from the reforming operation, the polymer gasoline (comprising that polymer normally produced plus the new polymer possible from the propylene-butylenes produced in the catalytic reforming operation) plus the available refinery butanes gave a 10.6 Reid vapor pressure product. The nominal results of these two operations on the given Mid-Continent refinery feed stock are compared in the following tabulations:

ASTM Octanes	Feed	Total Gasoline Desulf.	Reformed Blend
Clear	64.0	65.3	70.8
Plus 3 cc. TEL/gal.	77.9	81.3	83.6
Research Octanes			
Clear	66.9	68.2	75.3
Plus 3 cc. TEL/gal.	82.9	85.0	88.8
Reid Vapor Pressure	9.5	9.4	10.6
Yields, vol. %		99.5+	93.6

The improvement of this total refinery gasoline by either catalytic desulfurization or catalytic reforming is graphically shown in Fig. 2. By selective blending of this total gasoline regular and premium gasolines of 80 and 85 ASTM can be made without the use of excessive amounts of tetraethyl lead.

Equipment and Operation

The facilities employed in the Perco catalytic reforming process are schematically shown in Fig. 1. The feed stock, which may be any one or mixtures of several classes of products such as natural or straight-run gasolines, cracked gasolines, straight-run or cracked naphthas and cycling plant "distillates," is charged by a feed pump in heat exchange with the catalyst tower effluent, thence to a suitable process heater. From the process heater the superheated feed passes to one of the two catalyst towers at temperatures up to about 1050° F. and at pressures ranging up to 200 pounds gauge, depending, of course, upon the nature of the feed and the optimum operating conditions for such feed. After passing in heat exchange with the feed, the effluent is passed directly to the after-fractionating equipment for rerunning to end point and stabilization as desired.

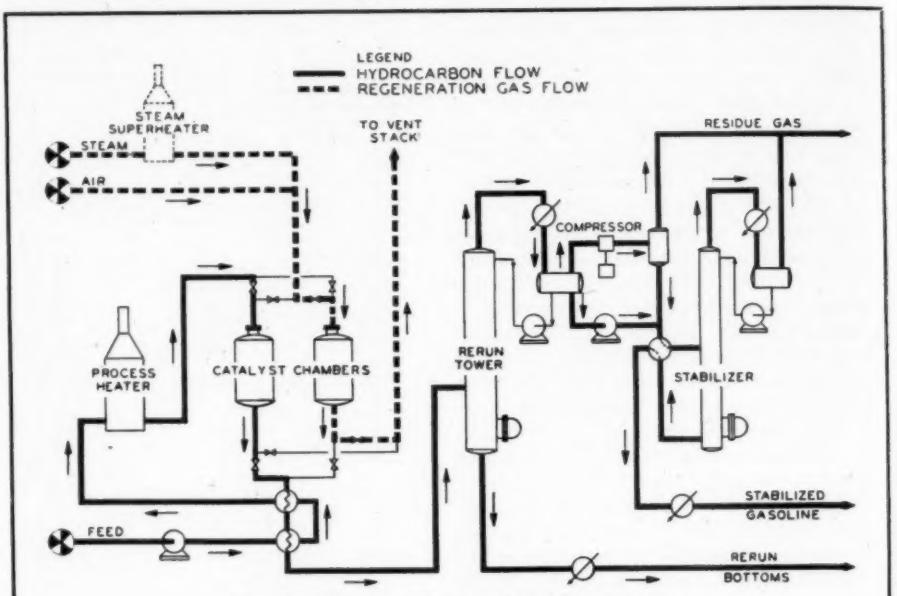

Fig. 1—Perco catalytic reforming process

To accomplish catalytic desulfurization as distinguished from catalytic reforming the temperature of operation is reduced to within the range of 650 to 850° F. Under such conditions and again depending upon the feed stock and its total sulfur content rerunning and stabilization may or may not be necessary.

Simultaneously with the process period just described the alternate catalyst tower will be on regeneration. The regeneration of this fixed bed, low-cost catalyst requires no special operating technique and is accomplished in the equipment illustrated by the broken lines in Fig. 1. Catalyst regeneration merely comprises burning in place carbonaceous deposits from the catalyst with air in admixture with superheated steam as a heat carrier to control the maximum temperature of regeneration within safe limits. The reactor is first purged with steam for a brief period and, without interrupting the flow of steam, air is admitted to the reactor at a predetermined rate to accomplish regeneration in the required period of time. Perco catalyst regeneration has been practiced satisfactorily in a commercial unit for a number of years. More recent units put into operation and those now under construction utilize the same scheme of operation.

The frequency of catalyst regeneration in either the catalytic reforming or desulfurization processes depends upon the amount of carbonaceous matter deposited on the catalyst. Among the various factors affecting carbon deposition are (1) nature of the stock (2) severity of operating conditions or the time-temperature relationship, and (3) length of process period. Carbon deposition increases in proportion to the time-temperature

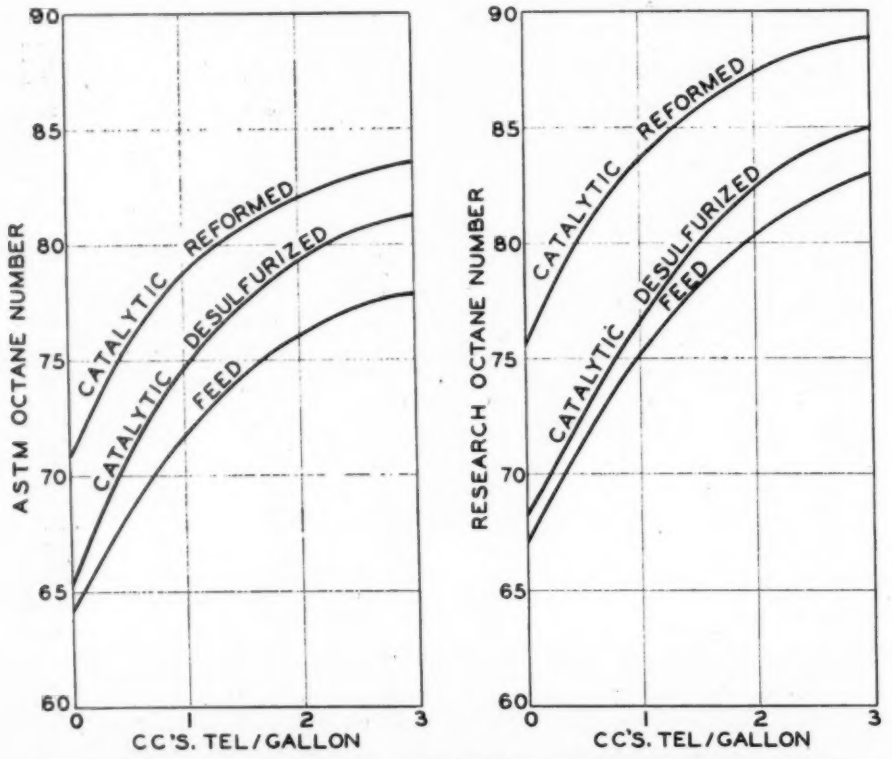

Fig. 2—Catalytic processing of a typical Mid-Continent total refinery gasoline

relationship for any given stock and for any given set of operating conditions is usually greater for cracked gasolines than for straight-run gasolines.

The necessity for regenerating facilities in connection with these installations is primarily dependent upon the catalyst cost. As a general rule regeneration equipment is not required for units designed specifically to desulfurize straight-run or natural gasolines, due to the fact that throughputs of 5000 to 15000 b/ton are realized. However, for the desulfurization of cracked gasoline and cracked-straight-run blends or catalytic reforming of any type stock, regeneration facilities are required.

Remarks

It is significant that Perco catalytic desulfurization and Perco catalytic reforming operations may be performed in the same equipment; there being no appreciable change in operating conditions except the catalyst case temperature. It has been shown that desulfurization of the separate streams or a blend of total refinery gasoline of either nominally high or low total sulfur content will result in considerable octane improvement at substantially no volume loss. As conditions require a further octane number improvement may be realized over that obtained by desulfurization merely by raising the temperature of operation to catalytic reforming conditions.

It is to be pointed out that these operations are quite applicable to refineries having catalytic cracking facilities for the reason that catalytic cracking as such is not applicable to stocks boiling within the motor fuel range. With every increase in the octane number specifications of motor fuels, the degrading effects of the relatively low octane straight-run fractions of any refinery become more and more pronounced, and as long as straight-run fractions are used in motor fuel blends the need for up-grading these stocks will remain a vital consideration.

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PERSONALS

Petroleum Technologists in the Headlines

William K. Warren, president of Warren Petroleum Corp., Tulsa, is the current recipient of the Hanlon Award, the highest honor conferred by the natural gasoline and cycling industries for outstanding service to those industries. His part in broadening and stabilizing the market for their products was cited in the presentation of the award, at the recent annual convention of the Natural Gasoline Assn. of America. "His sponsorship and financing of a huge storage program enabled many manufacturers to continue operating their plants in times when other demand for their products had reached the vanishing point", the citation read.

Mr. Warren

Mr. Warren, a native of Nashville, went to Oklahoma in 1916 and opened his own office in 1922, becoming the first sales representative dealing solely in products of natural gasoline plants. His company is now one of the largest producers and marketers of natural gasoline products in the world.

• • •

Hugh A. Hamilton, who has been supervisor of the process engineering department of the Cities Service butadiene plant in Lake Charles, La., has accepted a position with the chemical manufacturing department of General Mills, Inc. He is to be the technical superintendent of the new fatty acids and acid derivatives plant under construction at Kankakee, Ill.

• • •

Melvin H. Gertz, formerly with Humble Oil & Refining Company, has joined the staff of Robert L. Purvin, Consulting Chemical Engineers, Dallas.

Mr. Gertz

Mr. Gertz graduated from the University of Texas, where he received the B. S. and M. S. degrees in Chemical Engineering. After graduation he served in both the Laboratory and Technical Service Divisions of the Humble Baytown Refinery. With the Purvin organization, he will serve as a consultant in process engineering and process control for the chemical and petroleum industries.

Paul D. Barton has been named chief engineer of the manufacturing department of Sun Oil Co., succeeding **Clarence H. Thayer,** recently elected vice president in charge of manufacturing. Mr. Barton was formerly assistant manager of the engineering department.

• • •

P. D. Blackburn, has been named assistant general superintendent of Magnolia Petroleum Co.'s natural-gas and gasoline departments. His headquarters will be Dallas.

• • •

Robert M. Cokinda has been promoted from technical representative at Shell Oil Co., Inc., in New York, to division lubricants engineer in Baltimore.

• • •

Everett M. Barber, supervisor of the engineering research department of the Beacon laboratories of The Texas Co.; **Jay B. Malin,** mechanical engineer with The Texas Co.; and **Joseph J. Mikita,** director of the engineering laboratory of the petroleum-chemicals division of E. I. du Pont de Nemours Co. were awarded the Levy medals of the Franklin Institute at the institute's Medal Day ceremonies in Philadelphia, April 16. The awards were made for research in connection with the elimination of combustion knock.

The Texas City conflagration last month took a heavy toll of technical personnel. Of the refineries in the area, Republic Oil Refining Co. suffered the heaviest losses in the number of dead and missing.

Listed among Republic's missing and presumed dead were the following technical personnel: **W. R. Holmsten,** vice president; **J. D. Millender,** maintenance engineer; **R. H. McMeans, Jr.,** process engineer; **J. H. Tadlock,** senior engineer; **K. E. Webb,** junior engineer; **V. D. Fereday,** fire and safety chief; **W. M. Barger,** superintendent, light oils department; **J. O. Miller,** junior engineer, and **Rufus D. Jones,** machine shop foreman. Known dead are **William P. C. Voiles,** recently named refinery superintendent; **B. M. Stewart,** industrial relations supervisor, and **F. I. Lutteman,** engineer.

Pan-American Refining Corp. lists only the loss of one of its technical staff, **Maurice Neely,** laboratory supervisor, reported missing.

The Stone Oil Co. has listed as missing, **Myer Hurwitz,** superntendent, and **A. B. Emshoff,** engineer.

Dr. Theodore W. Evans has been appointed manager of the Emeryville, (Calif.) research laboratories of the Shell Development Co. He succeeds Walter J. Hund who died in Feb.

Dr. Evans joined the Emeryville staff in 1930 as a research chemist and was active in the early development of alcohols, ethers and esters from refinery cracked gases and in the development of the solvent extraction theory.

Mr. Evans

Before the war Dr. Evans was pioneering in the development of synthetic glycerin from petroleum. During the critical rubber shortage his studies led to early supplies of vital synthetic rubber by an exclusive Shell process.

• • •

Frederic A. Gokey, Jr., and **James T. Mullen** have been appointed assistant regional engineers at the Bayway refinery of Standard Oil Co. of New Jersey.

• • •

Harry Sutherland has been transferred to the New York offices of Shell Development Co. from the Emeryville, Calif. laboratories.

• • •

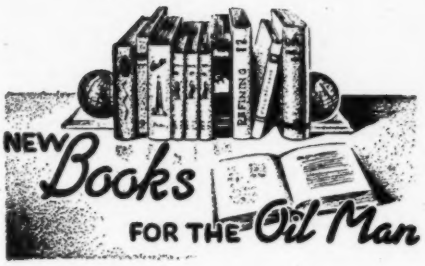
John E. Swearingen, group leader in the research department at Standard of Indiana's Whiting refinery has been transferred to the Stanolind Oil & Gas Co. at Tulsa. He will be replaced at Whiting by **Carl W. Peters.**

• • •

C. G. Kirkbride, former professor of chemical engineering at Texas A & M College, has joined the Houdry Process Corp. as director of the Houdry laboratories, and will make his headquarters at the laboratories near Marcus Hook, Pa.

Mr. Kirkbride

He taught chemical engineering at Texas A & M for two years after serving as chief of the chemical engineering and development department at Magnolia Petroleum Co.'s Dallas laboratories. His experience in the oil industry includes positions as assistant director of research for Pan American Refining Co., and as research engineer with the Standard Oil Co. (Ind.).



Copies of all books reviewed here may be ordered from the Reader's Service Department, Petroleum Processing, 1213 West Third St., Cleveland 13, for the prices listed, postpaid, unless indicated otherwise. Ohio purchasers please add 3% tax.

Discusses Synthetic Rubber's Part in National Economy

Buna Rubber, The Birth of an Industry, by Frank A. Howard, 5½ x 8½ in., 307 pages, indexed, stiff cloth binding, $3.75.

Buna Rubber is a case history of the synthetic rubber industry and its relationship to all American industry and economics. It records in a simple, straightforward manner the growth of Buna production from the days when the beginnings had to be made from foreign patents and research to its present stature of importance to the nation and to world trade.

Nobel prize winner Robert A. Millikan, in the introduction, says: ". . . The factual attitude and scientific objectivity which Mr. Howard has maintained throughout his narrative, in particular his freedom from caustic criticism in spite of the fact that the book lies in two highly controversial fields, international big business and governmental administration, gives it a unique value as a case history in the fields."

Author Howard was, from 1919 until his retirement in 1945, the principal executive of the Standard Oil Co. (N. J.) interests engaged in organizing and directing oil research, technical development, and chemical manufacturing activities.

Double Bonds Covered in First Of Polymer Research Series

Mechanisms of Reactions at Carbon-Carbon Double Bonds, by Charles C. Price, 6 x 9 in., 120 pages, flexible cloth binding, illustrated, indexed, $2.50 (1946).

Reactions at Carbon-Carbon Double Bonds is the first volume of a series of "Lectures on Progress in Chemistry" sponsored by the Institute of Polymer Research of the Polytechnic Institute of Brooklyn. The volume presents a series of lectures by the author at the Brooklyn Institute during the summer of 1945.

Subjects discussed comprise the electronic structure of unsaturated organic molecules, ionic reactions involving double bonds, free radical reactions involving double bonds, free radical addition polymerization, copolymerization, emulsion and suspension polymerization, and polar polymerization.

The author, Dr. Price, is Professor of Chemistry at the University of Notre Dame.

Several New Standards in 1946 ASTM Piping Specifications

ASTM Specifications for Steel Piping Materials, December, 1946, 6 x 9 in., 296 pages, heavy paper binding, $3.00.

In addition to all ASTM specifications covering steel piping and tubing, the December, 1946, compilation includes requirements on a number of other materials which are used in piping installations, such as castings, forgings, bolting materials, and nuts.

The book includes 14 specifications covering various types of pipe, ranging from ordinary carbon pipe for a variety of uses to high-alloyed steels for high temperature and pressure service. Thirteen specifications cover various types of boiler, superheater, and miscellaneous tubes, including four standards on stainless tubing.

Three specifications cover still tubes and a similar number pertain to heat-exchanger and condenser tubes. Five standards cover castings used in pipe installations, including valves, flanges, and fittings; there are four specifications covering forgings and welded fittings. Three standards cover carbon and alloy-steel bolting. In addition, there is included standard E19-46, concerning austenite grain size in steels.

New Text on Thermodynamics For Chemists Off the Press

Thermodynamics for Chemists, by Samuel Glasstone, 5¾ x 9 in., 522 pages, stiff cloth binding, illustrated, indexed, $5.00.

Thermodynamics for Chemists has been designed primarily as a textbook for college students of chemistry and chemical engineering. About 100 illustrative numerical problems are worked out in the text, and a total of about 360 problems are presented for solution by the reader.

In treating the various topics, the particular method used in each case has been chosen by considerations of simplicity, practicality, and logical approach. Whenever feasible, the generalized procedures, involving reduced temperatures and pressures are introduced. As regards statistical methods, the author feels that "the time has come for them to take their place as an essential part of chemical thermodynamics."

Consequently, the applications of partition functions to the determination of heat capacities, entropies, free energies, equilibrium constants, and the like have been introduced where their use is most praticable.

Author Glasstone was formerly research associate of Princeton University and Professor of Chemistry at the University of Oklahoma.

CLASSIFIED

Petroleum Processing announces this new classified section as a regular feature for the convenience of its readers. Classified rates are shown in the accompanying box.

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EDITORIAL COMMENTS

WIDENING HORIZONS

New Pattern for Refinery Operations

THE continuing large demand for petroleum products is setting up new conditions in plant operations, which in turn apparently will determine the economic pattern for the refining branch of the industry for an indefinite period into the future.

That refinery operations are to continue on a scale limited only by their ability to handle crude oil, where crude is available, is borne out by the latest statistical data. The efforts of operating forces will continue in the direction of straightening out production bottlenecks and keeping the plants running at the highest possible rates, to meet increased demand for the standard products except residual fuel oil.

This type of plant operation was accepted during the war, except that the emphasis was on producing aviation gasoline components. Wartime plant construction was almost entirely limited to aviation gasoline facilities. Very little was done to increase crude throughput capacity. It was anticipated that, when the war ended, plant capacity would be ample for some years and replacements and new construction could take place at a leisurely rate.

However, 1946 demand for products was very close to that of the peak of the war and latest estimates of the Economics Advisory Committee of the Interstate Oil Compact Commission are that 1947 demand will be 7% larger than the previous year. Demand is seen increasing for some years, barring a major business recession, due to the great expansion of practically all kinds of equipment which utilize petroleum. Therefore, refiners will be called upon to produce in addition to larger volumes of motor fuels, increased output of kerosine, heating oils, Diesel fuels and other products in the distillate fuels range. At least until new crude capacity is available, the refiners will be called upon to exercise their ingenuity to operate their primary distillation facilities to secure the largest possible volumes of fractions to further process into distillate products and motor fuels and to process heavier fuel oil cuts in their gasoline cracking units.

Another phase of the new economic pattern the refining industry is facing is the greater use of the products of natural gasoline, cycling and condensate plants to build up the supplies of motor fuels. Some indication of this is seen in the present expansion of these types of plants. Here the natural play of economics is working to bring about the conservation of the light petroleum hydrocarbons from natural gas more rapidly than would be possible by regulations of the state agencies.

Another angle in the pattern has to do with the financing of replacement and expansion facilities. The cost of such facilities will be much higher than before the war. One of the industry's leading economists recently said that the cost of a modern refinery with modern facilities to produce the improved products for today's markets would be two to three times that of similar prewar facilities. Refinery margins will have to be maintained on a basis that will provide for plant expansions being financed at least in part from earnings. As this same economist stated: "The oil industry, and the refining branch particularly, must adjust itself to some rather new and startling concepts of costs and margins".*

Octanes vs Conservation

COL. ERNEST O. THOMPSON, chairman of the Texas Railroad Commission, whose staunch advocacy of conservation of our petroleum supplies has gained him wide respect in the petroleum industry, has broadened his ideas of the field in which conservation should be practiced.

The average motorist gets no honest brass tacks value in added performance of his motor for the additional octane numbers above say 65 in motor cars up to and including the 1947 models, Colonel Thompson told the conventions of the Western Petroleum Refiners Assn. and the Natural Gasoline Assn. of America. Provided that proper adjustments have been made and the engine maintained in good order, octane numbers above 65 appear to be relatively unimportant, he said.

He went on to say that the refiner sacrifices from 1.5 to 2.5% of his potential total yield of gasoline for each increase of one octane number in the present range of fuels. "From the standpoint of the motorist, who is primarily interested in conservation as it affects motor fuel supply," he emphasized, "the best conservation program is one which will give the most miles per barrel or pound of crude."

Most people will agree with Colonel Thompson that the ultimate conception of petroleum conservation includes the efficient utilization of its potential energy. However, under our economy and free enterprise system we provide for the public's determining by its acceptance of products the extent to which our natural and industrial resources are to be utilized to its greater comfort and well being. To accomplish conservation by any other means, aside from education of the public, is on the order of rationing.

The public's preference for the improved motor fuels of today is shown in the almost entire lack of demand for third grade fuels, which would likely be of about the octane rating Colonel Thompson thinks we all should use. The trend in automotive engine developments over the years has been towards higher compression ratios requiring higher quality fuels, at higher cost to the public, for fundamental fuel economy and improved performance of cars. When the public thinks the improved performance isn't worth the added cost of gasoline and other car operating costs, the car manufacturers will be quick to feel it and reflect it in engine and car design.

Along this same line, another speaker at the NGAA meeting, W. M. Holaday, Socony-Vacuum Oil Co., Inc., said that manufacturers of equipment utilizing petroleum products should be cognizant of the fact that more stringent quality requirements will add to their cost and that compensation for such costs must be evident in comparable improvement in performance or economy to the equipment user.

"Manufacturers of automotive equipment should study the problem carefully," he stated, "and balance improvements in fuel economy through the use of higher compression ratios requiring higher quality fuel, as against the mechanism of decreasing weight of engines and vehicles and other innovations which will not require higher antiknock quality gasolines."

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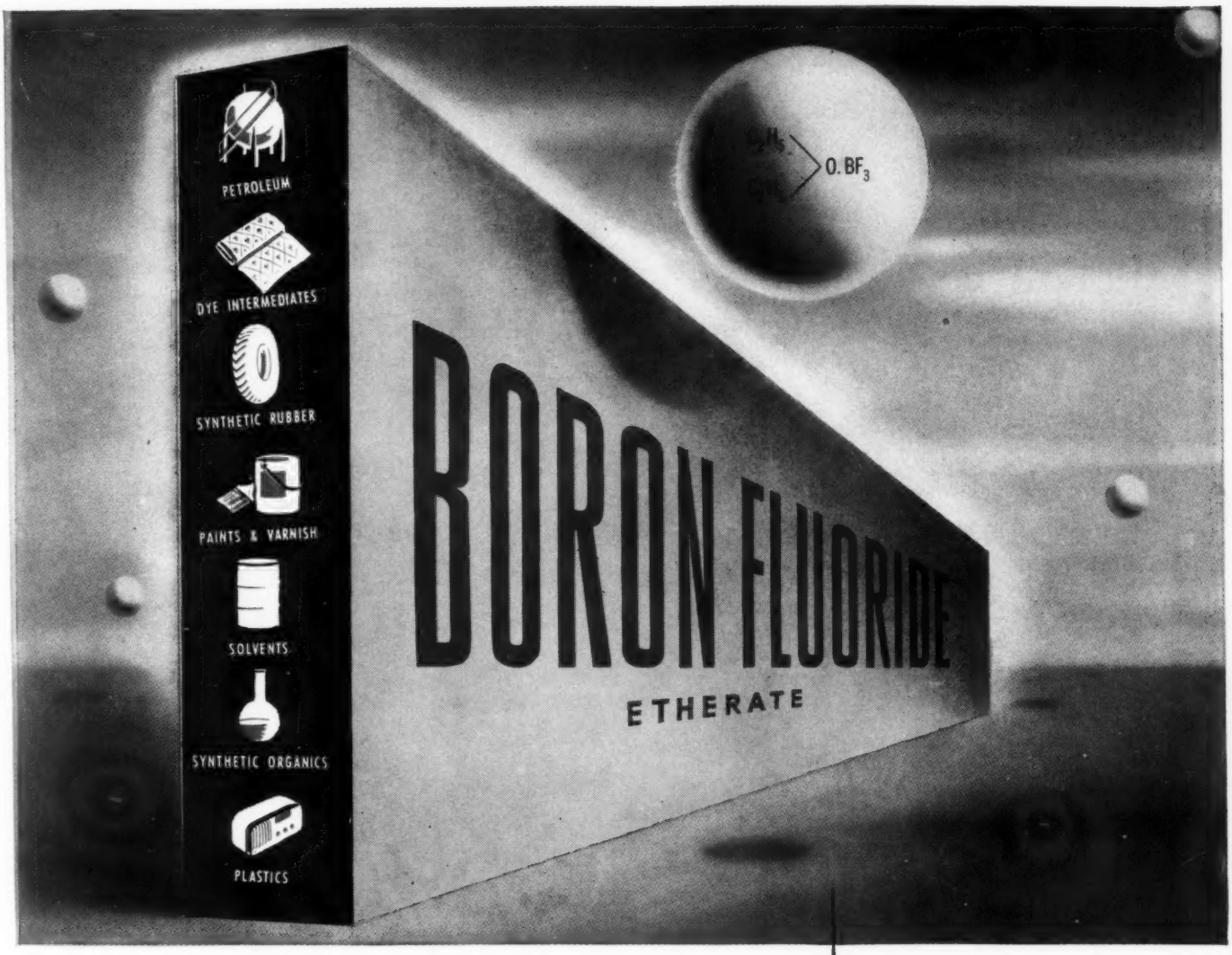
*"Various Aspects of Future Supply and Demand Problems", Sidney A. Swensrud, executive vice president, Standard Oil Co. (Ohio) before the Western Petroleum Refiners Assn., March 26, 1947.



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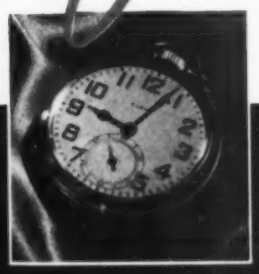

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